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THE

PHYSICAL REVIEW

THE ABSORPTION COEFFICIENTS OF HOMOGENEOUS X-RAYS BETWEEN WAVE-LENGTHS 0.1 A AND 0.71 A

By S. J. M. Allen

Abstract

Using the general radiation from a tungsten target, dispersed by reflection from a crystal, the total mass absorption in *fourteen elements of atomic number 6 to 83* (C, Mg, Al, S, Fe, Ni, Zn, Ag, Sn, W, Pt, Au, Pb and Bi) was determined for various wave-lengths from .10 A to .51 A by the ordinary ionization measurements. The Kα and Kβ radiation from a Mo target was used to give values for wave-lengths .63 A and .71 A. Very good agreement was found with the results of Richtmyer and Duane wherever these are comparable. For the elements from C(6) to W(74) the results are represented within a few per cent by the formula $\mu/\rho=\tau/\rho+\sigma/\rho=C\lambda^{2.92}N^{2.92}+\sigma/\rho$, where $C=7.82(10)^{-3}$ for the K absorption and $1.00(10)^{-3}$ for the L absorption and the scattering coefficient σ/ρ is assumed to increase with N from .144 for Al to .50 for W at .12 A, and also with the wave-length. The jump in the value of the fluorescent absorption coefficient τ/ρ from L to K absorption is the ratio of C_K to C_L or 7.8. The atomic absorption $\tau_a=2.18(10)^{-26}\lambda^{2.92}N^4$ (Bragg-Owens law). For the heavier elements Pt, Au, Pb and Bi the values of C_K get progressively lower to $4.7(10)^{-3}$ and those of C_L increasingly higher to $1.12(10)^{-3}$; the ratio or jump decreasing to 4.1 for Bi.

Introduction

An excellent summary of our knowledge of the absorption of x-rays when they pass through matter is given by A. H. Compton in the October, 1922, Bulletin of the National Research Council. On page 32 there is a table giving the mass absorption coefficients of a number of elements from Li to Pb for wave-lengths from .1A to 1.0A. For the most part these results are taken from the works of Hewlett,[1] Richtmyer,[2] and Duane[3] and are for homogeneous rays from a tungsten target reflected from a calcite crystal.

A careful examination of these results shows a considerable divergence of the mass absorption given by the different observers for the same

[1] C. W. Hewlett, Phys. Rev. **17**, 284 (1921)
[2] Richtmyer, Phys. Rev. **18**, 13, (1921)
[3] W. Duane, Proc. Nat. Acad., March 1922

substance and same wave-lengths. In the case of aluminum those of Hewlett are uniformly lower than those of Richtmyer. Those of Duane, over the short range investigated, agree well with those of Richtmyer. Only two results for the K absorption of an element of higher atomic number than that of silver are given, those of Hull and Rice[4] for lead, obtained eight years ago. It therefore seems desirable, considering the importance of the subject, to have a more complete set of absorption coefficients, comprising a greater range of wave-lengths and atomic numbers, especially the K absorption coefficients of the high atomic number elements. Experiments for this purpose have been carried out by the author during the last two years, and a summary of the results was given at the meeting of the American Physical Society at Cincinnati, December 1923. This paper gives the results and conclusions in a more detailed manner.

If a narrow beam of homogeneous x-rays passes through a layer of any substance whose thickness is d and density ρ the loss of energy is given by, $I_d = I_0 e^{-\mu d}$ where I_0 represents the energy on entrance, and I_d the energy on exit.

The quantity $\mu/\rho = (\log I_0 - \log I_d)/\rho d$, is known as the mass absorption coefficient. From μ/ρ can be calculated the atomic absorption coefficient μ_a by use of Avogadro's constant and the atomic weight.

The loss of energy represented by μ/ρ is due to the energy absorbed to produce the various fluorescent radiations represented by τ/ρ, and the energy lost by scattering etc. represented by σ/ρ.

Hence, $$\mu/\rho = \tau/\rho + \sigma/\rho$$

and, $$\mu_a = \tau_a + \sigma_a.$$

It has generally been accepted that these absorption coefficients can be represented empirically by the following expressions:

$$\tau/\rho = C\lambda^n N^p$$

$$\tau_a = C_a \lambda^n N^q$$

where λ is the wave-length in angström units; N the atomic number; C and C_a constants for each fluorescent series; n, p, q, empirical exponents.

Since μ/ρ alone can be measured by experiment it is necessary in some manner to assume values of σ/ρ, before τ/ρ can be estimated. In the range of λ from .1 A to 1.0 A, σ/ρ in general is a quite large part of μ/ρ, and for short wave-lengths and low values of N it is indeed the greater part, hence the uncertainty of σ/ρ renders confirmation of the formulas difficult. The most usual values accepted for the exponents are, $n = 3$, $p =$ nearly 3, and $q = 4$.

[4] Hull and Rice, Phys. Rev. **8**, 836 (1916)

When for any substance a wave-length is reached which is very close to its emission wave-length Kγ, the absorption coefficient suffers a very abrupt change, becoming 8 times as great in the case of passing from L to K. If the value of $(\tau/\rho)_K$ for the K absorption just after this change takes place is known, and the value of $(\tau/\rho)_L$ for the same wave-length which would have been observed if this change had not taken place is also known, we can divide $(\tau/\rho)_K$ by $(\tau/\rho)_L$ and obtain what we may call the "jump" J from L to K series. If the above formulas are sufficient to represent the values of $(\tau/\rho)_K$ and $(\tau/\rho)_L$ over the complete possible range of N, this jump should always be the same, about 8, and consequently C_K and C_L should be constants.

Experimental Arrangements

The modern method of measuring the absorption coefficients of homogeneous rays is well standardized, and it is not necessary to go into details here. The present work follows closely the methods used by Richtmyer and Duane.

A fine beam of the general radiation from a Coolidge Universal Tungsten tube was reflected from the (100) planes of a selected crystal mounted on a Bragg x-ray spectrometer. Both calcite and rock-salt crystals were used.

The resulting narrow spectrum was intercepted by a fine slit in the ionization chamber which was filled with methyl iodide vapor. Readings were carried out as follows. The zero position of the spectrometer was carefully determined by setting on the Kα lines of Tungsten and also on the Kα and Kβ lines of a Mo water-cooled tube. The tube was then excited to the desired voltage and the ionization chamber set to receive the definite wave-length to be tested. From the chamber angle 2θ, and the crystal spacing d, the value of λ was calculated from Bragg's classical equation $N\lambda = 2d \sin\theta$.

Ionization readings were then taken both before and after an absorbing layer was placed in position between the target and the crystal. For any wave-length chosen, a complete absorption test to extinction was always made on some substance, such as aluminum or copper. By plotting the log I against the thickness of layer, a resulting straight line would ensure that all corrections had been made, and one would be sure that he was dealing with a pure homogeneous radiation. Then, keeping this wave fixed in position and the voltage constant, measurements were made on all the other elements.

This method was used with all the wave-lengths observed from $\lambda = .1$ A to $\lambda = .5$ A. The measurements at $\lambda = .63$ A and $\lambda = .71$ A were

made with the Mo tube the α line being observed in the first, second, and third orders, and the β line in the first and second orders.

Instrumental errors should not be greater on the average than 1 per cent. The chief difficulty, as has also been mentioned by Richtmyer, is to obtain very thin layers of the high atomic weight elements which are homogeneous. In all cases the mass of matter traversed was obtained by weighing a layer of known area.

Results

The values of μ/ρ obtained in these experiments are shown in Table I. In Fig. 1 are plotted the results for the light elements C to S, in Fig. 2 those for the heavier elements Fe to Ag.

Table I

Mass absorption coefficients μ/ρ

Wave-length	C	Mg	Al	S	Fe	Ni	Cu	Zn	Ag	Sn	W	Pt	Au	Pb	Bi
.100A									1.04		3.80	3.40	3.60	3.40	2.90
.110			.165		.32	.37	.39	.46	1.23	1.50	4.36	4.10	4.20	3.92	3.50
.120	.148	.160	.175	.20	.38	.44	.47	.54	1.52	1.80	5.00	5.10	4.85	4.64	4.40
.130		.165	.185	.22	.43	.51	.56	.64	1.82	2.20	5.85	6.30	5.90	4.00	2.52
.138	.150	.170	.190	.24	.49	.57	.63	.74	2.15	2.55	6.70	7.30	6.00	2.90	2.20
.150		.175	.205	.27	.58	.67	.78	.89	2.63	3.00	8.10	4.30	3.60	2.37	2.44
.162	.152	.190	.218	.31	.68	.80	.94	1.06	3.18	3.60	5.00	2.60	2.63	2.78	2.90
.170	.155	.198	.228	.32	.70	.95	1.05	1.20	3.58	4.00	3.32	2.84	2.88	3.10	3.32
.180		.207	.243	.35	.82	1.10	1.22	1.36	4.10	4.70	2.53	3.24	3.30	3.52	3.86
.190	.160	.220	.256	.38	.93	1.27	1.40	1.57	4.70	5.40	2.76	3.70	3.76	4.00	4.42
.200		.232	.275	.42	1.07	1.45	1.55	1.77	5.50	6.30	3.20	4.16	4.28	4.64	5.10
.220	.165	.260	.310	.50	1.40	1.87	2.00	2.32	7.40	8.30	4.20	5.25	5.50	5.90	6.48
.240	.169	.293	.356	.58	1.75	2.28	2.50	2.80	9.60	10.8	5.10	6.65	6.95	7.40	8.30
.260		.330	.410	.68	2.22	2.83	3.05	3.50	12.2		6.10	8.00		9.50	10.4
.280	.182	.375	.475	.80	2.75	3.38	3.70	4.30	14.8		7.20	9.60		11.5	12.5
.300	.190	.430	.545	.93	3.30	4.10	4.50	5.10	17.9		8.60	11.5		13.6	14.8
.320	.200	.480	.630	1.08	3.95	4.87	5.25	6.20	21.1		10.1	13.5		16.2	17.7
.340	.210	.570	.730	1.23	4.65	5.75	6.38	7.30	24.5		12.0	15.8		19.7	21.0
.360	.216	.660	.850	1.42	5.40	6.70	7.55	8.50	29.2		14.5	18.2		23.0	
.380	.230	.760	.970	1.58	6.25		8.80	10.0	34.0		17.0	21.2		27.2	
.400	.245	.875	1.11	1.78	7.25		10.2	11.6	38.2		19.8	24.5		31.8	
.420	.260	.995	1.25	1.95	8.30		11.7	13.5	43.5		22.8	28.0		36.5	
.440	.275	1.13	1.41				13.2	15.4	49.5		26.5	31.8		41.2	
.450	.282	1.20	1.48				14.0	16.4	53.0		28.0	33.5		43.5	
.460	.291	1.27	1.56				14.9	17.5	37.0		30.0	36.0		46.5	
.484	.312	1.44	1.75				17.2	20.2	8.8		34.3	41.5		53.0	
.500			1.94				19.0	22.0	10.5		38.0	45.5		58.0	
.630	.55		3.78	6.9			37.8	43.0	20.5		75.0	87.0		101.	
.710	.68		5.35	9.9			53.7	60.0	28.5			119.		140.	

These results cover a range of λ and N which is about the same as investigated by Richtmyer, Hewlett, and Duane. There is extremely good agreement between the results of the author and those of Richtmyer, and also those of Duane in the case of Al, Cu, and Ag. The results for C agree well with those of Hewlett at short wave-lengths, but are generally higher than his at longer wave-lengths. All elements show a steady but slower decrease as λ approaches .1 A. There is no indication as yet of any abrupt change. In Figs. 3 and 4 are plotted those portions of the results for the high atomic number elements W, Pt, Au, Pb, and Bi between .10 A and .24 A, which include the critical absorption wave-lengths Kγ. It is to be noticed that the observations are carried right through the abrupt changes of μ/ρ.

These results for high weight elements show very clearly a distinct difference from similar results for lower weight elements. For example, if we compare the results for W and Bi, we see that in the L absorption

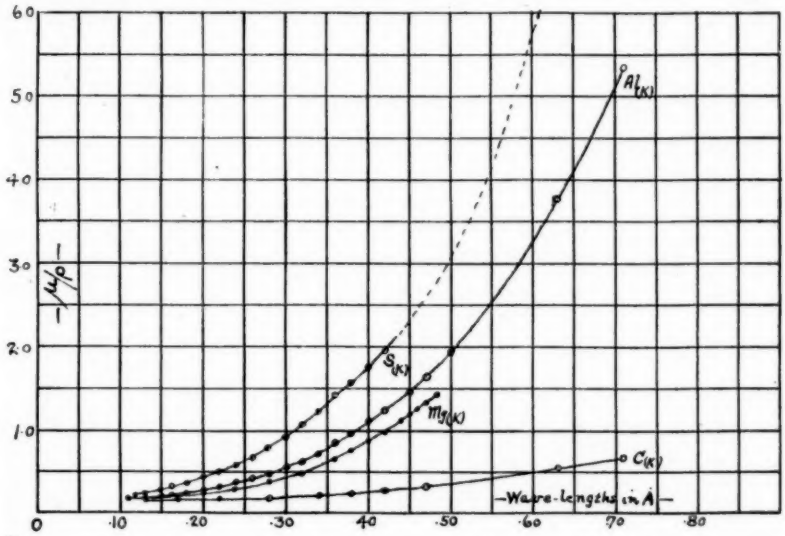


Fig. 1. μ/ρ as a function of wave-length for C, Mg, Al and S.

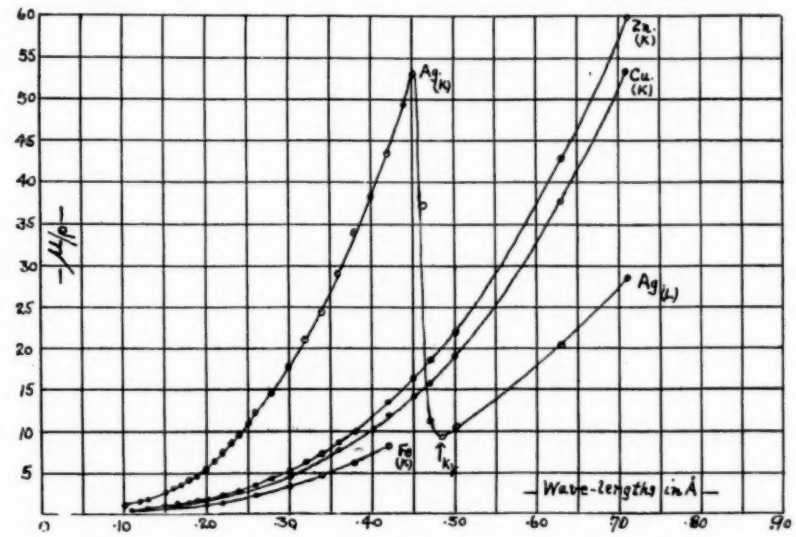


Fig. 2. μ/ρ as a function of wave-length for Fe, Cu, Zn and Ag.

the graphs for Bi lie above that for W in accordance with the order of the atomic numbers, but in the K absorption this is reversed. The same phenomenon is true for all the heavy elements. In short, the sudden rise, or "jump" from L to K absorption is much less than would be

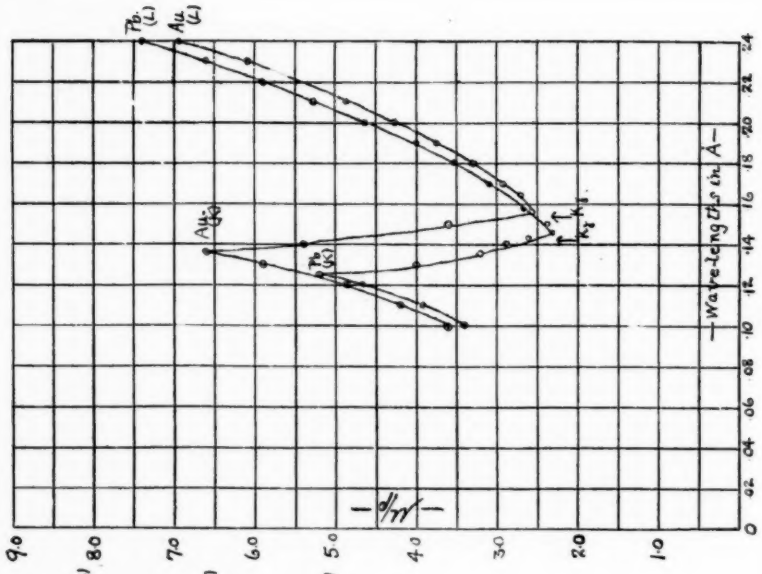


Fig. 4. μ/ρ as a function of wave-length, for Au and Pb.

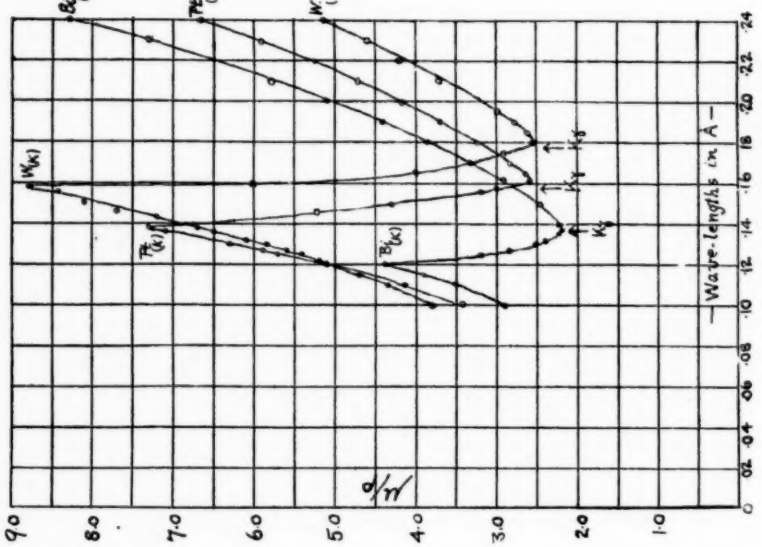


Fig. 3. μ/ρ as a function of wave-length, for Bi, Ptand W.

predicted by extrapolation of the formulas given above, and moreover this jump becomes progressively less as N increases.

In Table II are shown these "jumps" J calculated from the graphs and corrected for scattering from assumed values of σ/ρ.

The values of $(\tau/\rho)_K$ are the highest K values experimentally obtained and λ is the wave-length at which they occurred. The values of $(\tau/\rho)_L$ are those at the same wave-length of the L absorption which would have been obtained if the "jump" had not occurred. With the high weight atoms are included also Ag, Mo (from Richtmyer) and Cu (from Barkla).

TABLE II

Relations between the K and L absorption coefficients at the absorption limit Kγ

Element	N	λ	$(\mu/\rho)_K$	σ/ρ	$(\tau/\rho)_K$	$(\mu/\rho)_L$	$(\tau/\rho)_L$	J
Cu	29	1.46 A	440	—	440	55	55	8.0
Mo	42	.60	81	.40	80.6	11.0	10.6	7.6
Ag	47	.45	53.5	.45	53.0	7.5	7.0	7.5
W	74	.159	9.00	.55	8.45	1.95	1.40	6.0
Pt	78	.138	7.35	.63	6.72	1.90	1.27	5.3
Au	79	.136	6.65	.64	6.01	1.85	1.21	5.0
Pb	82	.125	5.25	.69	4.56	1.70	1.01	4.5
Bi	83	.120	4.40	.70	3.70	1.60	.90	4.1

It is readily seen that, while this "jump" in the absorption coefficients in passing from the L to the K levels is approximately 8 times for light elements, it becomes progressively less as N increases, showing a quite rapid decline from $N=74$ to $N=83$.

The values of J here given depend upon the values of σ/ρ assumed and, since we have no very exact knowledge of σ/ρ for high weight atoms, they can be considered at this stage as only approximate. There seems, however, no doubt that they progressively decrease with the increase of N.

Whether the absorption coefficients change so abruptly as to constitute a discontinuity is open to question. The results here indicated with high atomic number elements would seem to show that the abrupt rise slants backward towards shorter wave-lengths and that actual measurements can be made in this changing region, even with slit widths of .1 to .2 mm.

At the same meeting mentioned above, Richtmyer read a paper on the relations of the absorption coefficients in the immediate neighborhood of the K critical absorption, which showed results almost identical with those of the author, confirming the idea that the value of J decreases steadily with the increase of N.

A very careful analysis of all the values of μ/ρ in this work was made to test the accuracy of the empirical formulas discussed above. This was done by actual calculation by trial and error instead of the method usually employed of plotting μ/ρ against N^3. It was found that, if

suitable values of σ/ρ were chosen, over a wide range of λ and N up to 47, the fluorescent absorption coefficient τ/ρ could be expressed by a formula of the form,

$$\tau/\rho = C\lambda^n N^p,$$

and the atomic coefficient by

$$\tau_a = C_a\lambda^n N^q.$$

σ/ρ was taken for Al at $\lambda = .12$ A as .144 and at $\lambda = 1.0$ A as .20, with increasing values as N increased.

It was found that on the average $n = 2.92$ (instead of the usual value 3), $p = 2.92$, and $q = 4$ best fitted the results.

TABLE III

Empirical data with reference to $\tau/\rho = C\lambda^{2.92}N^{2.92}$ *and* $\tau_a = C_a\lambda^{2.92}N^4$

Element	N	σ/ρ at $\lambda = .12$A	C_K ($\times 10^{-3}$)	C_L ($\times 10^{-3}$)	$(C_a)_K$ ($\times 10^{-26}$)	$(C_a)_L$ ($\times 10^{-26}$)
C	6	.145	7.76		2.21	
Mg	12	.144	7.48		2.05	
Al	13	.144	7.82		2.19	
S	16	.15	7.92		2.10	
Fe	26	.16	7.67		2.10	
Ni	28	.17	7.85		2.08	
Cu	29	.18	7.73	.97	2.14	.267
Zn	30	.20	8.02	1.02	2.20	.279
Mo	42	.28	7.47	.97	2.09	.269
Pd	46	.32	7.81	1.02	2.20	.287
Ag	47	.35	7.73	1.00	2.15	.275
Sn	50	.40	7.43	1.00	2.13	.288
W	74	.50	7.66	1.00	2.23	.290
Pt	78	.58	6.71	1.04	1.96	.304
Au	79	.60	6.33	1.03	1.84	.301
Pb	82	.67	5.42	1.08	1.59	.302
Bi	83	.70	4.71	1.12	1.37	.324

Extrapolation of these formulas to high atomic weight elements for the K series gave predicted values much higher than those actually measured. The accord was better in the case of the L absorption. The complete data are shown in Table III. The results for Mo are taken from Richtmyer and those for Sn from Bragg and Pierce. The universal constant $(C_a)_K$ is $= 2.18 \times 10^{-26}$ for $N = 2.92$ (K absorption) and $(C_a)_L = .29 \times 10^{-26}$ (L absorption). $C_K = 7.82 \times 10^{-3}$, and $C_L = 1.0 \times 10^{-3}$.

It would seem that these formulas do not hold throughout the whole range of λ and N, and certainly not near a critical absorption region.

Very notable attempts to deduce a theoretical formula for τ_a have been made recently by De Broglie[5] and by H. A. Kramers[6] on the quantum theory. Both of these formulas indicate a decrease to be expected in J as N increases, which would be in accord with the results of this paper.

UNIVERSITY OF CINCINNATI,
January 25, 1924.

[5] L. de Broglie, Jour. de Phys. et Rad. 1922

[6] H. A. Kramers, Phil. Mag. Nov. 1923

THE K AND L ABSORPTION AND EMISSION SPECTRA OF TUNGSTEN

By C. B. Crofutt

Abstract

Both the absorption and emission spectra were photographed simultaneously on the same plate, using a special float-operated mechanism to turn the crystal very slowly so as to obtain the faint lines between β_2 and β_5. The *absorption wave-lengths* were found to be: LA_1, 1.2122A; LA_2, 1.0716A; LA_3, 1.0217A; KA, .17802A. Table I gives the *emission wave-lengths* of 28 L emission lines including the four new lines β_{15} (1.2432), β_{16} (1.2166), γ_{12} (1.0748) and n (1.0699), and of the Kβ_3 line (.18525) which is the line found by DeBroglie. *Comparison with the Bohr theory.* The agreement of the emission frequencies computed from the energy levels with the measured wave-lengths is better than 1/10 per cent, except for β_{15} and β_{16}. The lines β_{10}, β_9, γ_{12}, and γ_{11}, however, correspond to transitions between energy levels which are not predicted by the selection principle, and lines β_8 and n are not in agreement with the accepted energy levels. While Ln may be due to an impurity, β_8 is probably a tungsten line.

THIS work is an investigation of the absorption and emission spectra of tungsten under the same experimental conditions. Both spectra were obtained simultaneously on the same photographic plate in order to make certain the relative positions of the absorption limits and the emission lines.

Experimental Method

A medium focus tungsten target Coolidge tube was used as a source of x-rays. The x-rays were analyzed by means of a rock salt crystal and the spectra were recorded on photographic plates. The apparatus is essentially that used by Dershem[1] with the substitution of an accurately constructed crystal table, a narrow slit of 0.005 cm width, and a new rotator for the crystal.

The crystal table is shown in Fig. 1 and consists of a spindle fitted in bearings as shown. This spindle is removable and additional spindles make it possible to change crystals without remounting each time.

The crystal was rotated through a small angle by means of levers attached to a float in a tank of water, the level of which was raised by means of a small stream of water and lowered by the use of an intermittent syphon. The advantage of this method is that the crystal can be set for a particular line and a prolonged exposure taken with the as-

[1] Dershem, Phys. Rev. **11**, 461 (1918)

surance that the crystal will not rotate too far. The rotation can be made as slow as desired and the angle kept as small as a quarter of a degree. The fine slit greatly prolongs the time of exposure but enables greater resolving power to be obtained. The fine slit and the rotator made it possible to obtain the group of faint lines between β_2 and β_5.

While working with the L series it was necessary to keep the voltage so low that no appreciable second order continuous radiation would affect the plate at the same point.

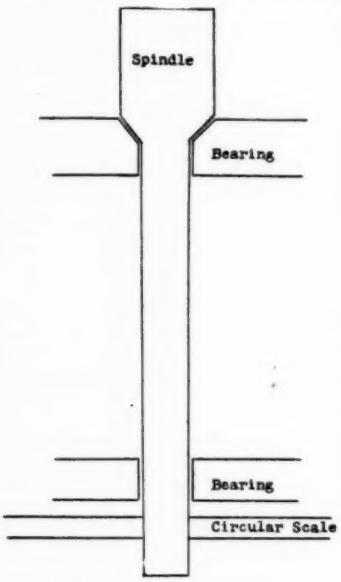


Fig. 1. Crystal table.

The work on the K series was done in the third order using 110,000 volts, effective value. The first and second order radiations were removed by absorbing screens.

The absorption bands were obtained by placing a screen of tungsten oxide in the path of the beam before it entered the spectrometer. This in no way interferes with the production of the emission spectra but does interfere with the analysis as emission lines are close to the absorption bands.

The method of measuring the plates is that developed by Dershem[1] in which a correction is made for the width of the slit. Measurements of faint emission lines and absorption bands were always made relative to strong emission lines.

Corrections

With the method employed there are two chief sources of error.

(a) If the plate is not perpendicular to the line of collimation it can be shown from geometrical considerations that θ is given by the following formula

$$D \tan 2\theta = d\sqrt{(1+m^2)} \pm \sqrt{d^2(1+m^2)+D^2m^2},$$

where θ is the glancing angle, d the distance from the crystal to the plate, D the distance between the lines as photographed on both sides of the line of collimation, and m the tangent of the angular displacement of the normal to the plate from the line of collimation. Since this correction is small, m may be determined with sufficient accuracy by means

of two known lines. In a manner similar to the above it can be shown that

$$2(1-p)m=(1+p)(m_1+m_2)\pm\sqrt{(1+p)^2(m_1+m_2)-4(1-p)^2m_1m_2}$$

where p is the ratio of the distances between the two lines on opposite sides of the line of collimation, m_1 and m_2 the value of $\tan\theta$ for the two known lines.

(b) If the face of the crystal is not in the axis of rotation an amount equal to $\delta/\sin\theta$ must be added to or subtracted from the distance from the axis of rotation to the plate in order to obtain the distance from the crystal to the plate, where δ is the displacement of the face of the crystal from the axis of rotation. Since for small values of θ, $\sin\theta$ is small this correction is important.

TABLE I

Wave-lengths in Angstroms

L SERIES

α_2	1.4844	β_{15}	1.2432	β_{10}	1.2099	A_2	1.0716
α_1	1.4733	β_2	1.2421	β_9	1.2027	n	1.0699
η	1.418	β_8	1.2364	γ_2	1.1299	γ_2	1.0659
β_4	1.2988	β_7	1.2217	γ_1	1.0964	γ_3	1.0599
β_6	1.2875	β_{16}	1.2166	γ_8	1.0786	γ_{11}	1.0444
β_1	1.2793	β_5	1.2133	γ_{12}	1.0748	γ_4	1.0266
β_3	1.2602	A_1	1.2122	γ_6	1.0723	A_3	1.0217

K SERIES

Comparison lines				Measured			
α_2	.21352	β	.18436	β_3	.18525	A	.17802
α_1	.20885	γ	.17940				

Using Dershem's method for locating the lines, the penetration into the crystal does not introduce an error for the method depends on locating the edge of the line as reflected from the face of the crystal.

EXPERIMENTAL RESULTS

Table I shows the experimental results on the emission and absorption in the L and K series. The absorption limits are indicated by the letter A with appropriate subscript. In the L series the following lines were measured carefully and the results taken as standards for the measurements of all other lines: α_1, β_1, β_2, γ_1, γ_3, and γ_4. The comparison lines in the K spectrum are indicated in Table I. Because of the presence of the reference lines the results obtained on two or more plates varied only in the last significant figure shown. The line l does not appear because of the absorption in the glass walls of the tube. The lines β_{15}, β_{16}, γ_{12}, and n are new lines for the L series of tungsten.

Discussion of Results

Fig. 2 presents the results in the well known form of energy levels as recently published by Bohr and Coster.[2] Table II gives the corresponding frequencies of the energy levels. The K and L frequencies were obtained directly from the measurements made on the wave-lengths. The other

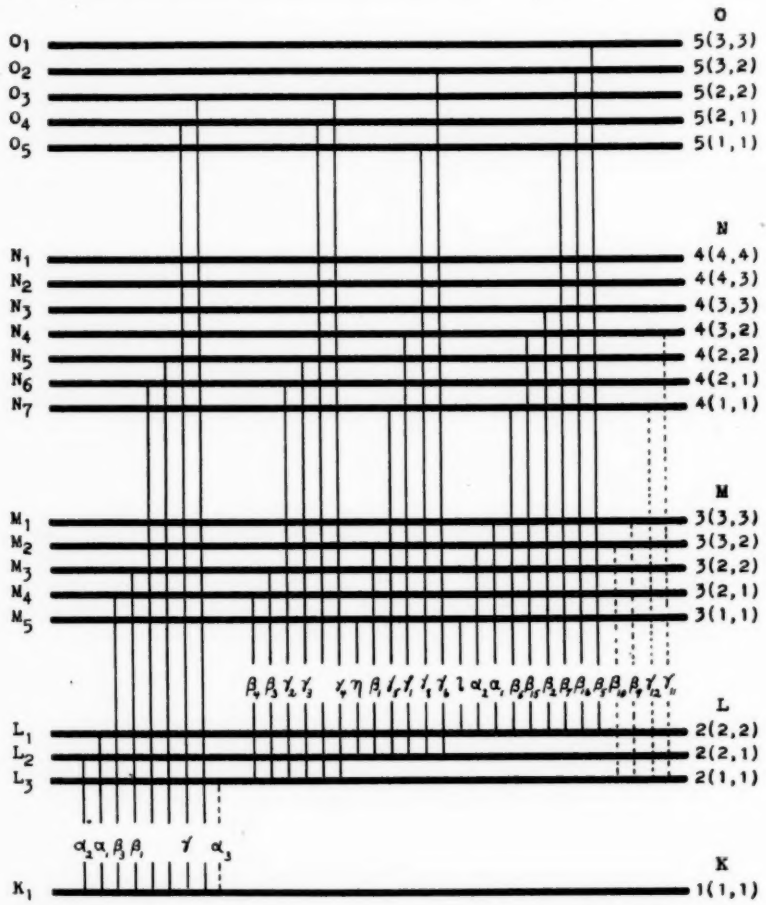


Fig. 2. Energy level diagram for tungsten showing the K and L series. Solid lines are transitions predicted by the selection principle. Broken lines are other transitions.

frequencies were calculated from the K and L absorption frequencies and the frequencies of the emission lines. The solid lines between the energy levels of Fig. 2 represent transitions predicted by the selection principle.[3]

[2] Bohr and Caster, Zeits. f. Phys. **12**, No. 6 (1923)

[3] Bohr, Phil. Mag. June 1922

The broken lines represent other transitions found. The notation is that of the line produced by the transition. If there is no symbol the line has not been found. The symbols at the left of the horizontal lines are the usual notations of the energy levels; those at the right are the notations of Bohr and Coster [the symbol 4(2,1) corresponds to the energy level having the total quantum number 4, the "grund" quantum number 2 and the azimuth quantum number 1].

The selection principle states that the azimuth quantum number must change by ± 1 or 0 and that the "grund" quantum number must change by ± 1.[2]

TABLE II

Absorption frequencies $\times 10^{-18}$

K and L measured; M, N and O calculated

K_1	16.844	M_1	.4401	N_3	.0579	O_1	.0022
L_1	2.4738	M_2	.4548	N_4	.0629	O_2	.0053
L_2	2.7982	M_3	.5554	N_5	.1058	O_3	.0140
L_3	2.9349	M_4	.6261	N_6	.1220	O_4	.017
		M_5	.6814	N_7	.1448	O_5	.0189

A comparison of Table I with Fig. 2 shows that all but the β_8 and n lines are represented on the diagram. The n line is a new line and may be due to some impurity, although a comparison with tables failed to reveal its identity. The β_8 line has been found by Overn[4] and Siegbahn[5] and should be accepted as a line of tungsten. This line is hard to measure being very indistinct. Coster[6] has shown that it appears as β_{11} and β_{12} in elements of atomic numbers 47 to 51. Of the four lines of the L series β_9, β_{10}, γ_{11}, and γ_{12} not given by the selection principle, γ_{12} is a new line. A careful investigation failed to reveal the $K\alpha_3$ line of which Duane and Shimizu[7] found some indication. The results indicate that if it does exist it does not differ in wave-length from the α_2 line by more than .04 per cent, or else its intensity is so low that it is concealed by the general radiation. It is not predicted by the selection principle. The two other new lines are given by the selection principle.

β_{15} is so close to β_2 that it could not be completely resolved, but because of the difference in intensity the edges of both lines could be located and measured. The other new lines are very faint and close to lines already known. $K\beta_3$ is the line previously found by DeBroglie.[8] The wave-lengths obtained for the absorption bands are shorter than those

[4] Overn, Phys. Rev. **14**, 137 (1919)
[5] Siegbahn, Phil. Mag. Nov. 1919
[6] Coster, Phil. Mag. Sept. (1922)
[7] Duane and Shimizu, Phys. Rev. **14**, 67 (1919)
[8] De Broglie, Comptes Rendus, 1920

obtained by Duane, which are usually accepted as standard. These changes in wave-length are sufficient to alter the relative positions of the LA_1 and the LA_2 with respect to β_5 and γ_6, as is shown in Table III and of course visually on the plates themselves.

It is seen from Fig. 2 that all lines found as transitions between energy levels but not predicted by the selection principle involve (1,1) energy levels. This may be a coincidence but it may have significance.

No special attempt was made to obtain the relative intensities of the lines. The β_{15} is of medium intensity while the other new lines are very faint.

The fact that the lines β_{15}, β_{16}, and γ_{12} fit into the energy level diagram makes it seem reasonable that they are tungsten lines.

Since the absorption and emission spectra appear on the same plates it is impossible to say much regarding the structure of the absorption bands, some of the emission lines being very close to the absorption edges. However the edges were sharp and easily measured.

TABLE III

The shift in absorption wave-lengths

A_1	1.2140*	A_2	1.0730*	γ_4	1.0266
β_2	1.2133	γ_6	1.0723	A_3	1.024*
A_1	1.2122	A_2	1.0716	A_3	1.0217

The differences between the frequencies of the emission lines as computed (1) from the energy levels and (2) from the measured results are about .13 per cent for β_{15} and β_{16} and less than .10 per cent for the remainder with an average difference of .03 per cent.

CONCLUSIONS

The selection principle reduces the possible number of lines from fifty-one to twenty-one for the L series and from twenty to eight for the K series. Two of the new lines found agree with the selection principle, thus increasing the total number in agreement from eighteen to twenty for the L series, leaving one more line to be found. All lines in the K series are in agreement with the principle.

In addition to the lines given by the selection principle four were found in the L series which are not in agreement but which quantitatively correspond to transitions between energy levels. The $K\alpha_3$ line, found by Duane but not observed by the present photographic method, is not in agreement with the selection principle and is yet somewhat in doubt.

As an indication that the present energy levels are not sufficient there appear to be two lines in the L series which are not in agreement. One

*Values given by Duane and Shimizu[7]

of these is a new line and may be due to an impurity; the other is the β_8 line.

It is seen from the above that the energy levels as drawn do not satisfy all the measurements of what are undoubtedly tungsten lines, and that Bohr's selection principle would eliminate four lines which have been found. These disagreements emphasize the need for further experimental and theoretical work.

I wish to acknowledge indebtedness to the members of the staff of the physical laboratory at the University of Iowa for their interest in the work and especially to Professor G. W. Stewart who suggested the problem.

UNIVERSITY OF IOWA.
February 27, 1924.

THE CONSTITUTION OF GASEOUS IONS

By J. J. Nolan

Abstract

Mobilities of various groups of ions in dry and moist air.—Using the Franck modification of the Rutherford alternating current method, with the plate and gauze accurately parallel and 2.5 cm apart, current-voltage curves were obtained as the 52 cycle voltage was increased from 200 to 500 volts. Previous experiments have shown the presence of four predominating types of positive ions with mobilities of 2.04, 1.73, 1.52 and 1.34. The curves now reproduced show periodic inflections about every 10 volts which indicate intervening groups making some twenty groups of ions with mobilities varying from 2.24 to 1.34. These values agree closely with those computed according to *J. J. Thomson's theory for clusters* of from 15 to 36 water-molecules. In dry air the groups with the lower mobilities are less prominent. Other experimental evidence is cited in favor of the cluster theory as opposed to the small ion theory of ions. Loeb's criticism of the author's work is discussed and it is shown that there is no real divergence between these results and those of Loeb.

THE constitution of the ions in gases at normal pressures is still a matter of controversy. In various papers[1,2,3] the present writer has brought forward evidence which, if accepted, would be decisive in favor of the older cluster theory as against the more recent view which regards the gaseous ions as simply charged molecules. It was claimed that these experiments demonstrate that the normal ionization consists of a mixture of distinct groups having mobilities not widely different from one another, and that in addition there are present in small numbers groups of ions of much higher mobility. These conclusions have been contested by Loeb[4] who holds that his experiments demonstrate the existence of only one type of ion. He is of opinion that results which suggest a complex ionization are spurious and are due to "failure to observe some of the fundamental conditions" of successful experiment. The object of the present paper is, firstly to describe fully the apparatus and the experimental method used by the author so as to permit of criticism on that head being definite; secondly to show that the results of Loeb when properly interpreted, not merely do not controvert but actually support

[1] J. J. Nolan, Proc. Roy. Irish Acad. **35**, 38 (1920)
[2] J. J. Nolan, Proc. Roy. Irish Acad. **36**, 74 (1923)
[3] J. J. Nolan and J. T. Harris, Proc. Roy. Irish Acad. **36**, 31 (1922)
[4] L. B. Loeb, Journal Franklin Inst. **196**, 537 (1923)

the contentions of the present writer; and finally to bring forward further evidence as to the structure of ions in air.

Apparatus and Experimental Methods

The method of measuring ionic mobilities employed in the work under discussion is the well-known modification of Rutherford's method due to Franck. Ions are produced on one side of a metallic gauze and those of one sign are driven by a steady field through the gauze. Here they come under the influence of an alternating field of sine form between the gauze and a parallel plate. If the potential difference is such that its value read on an electrostatic voltmeter is greater than $\pi n d^2/\sqrt{2}u$ where n is the frequency, d the distance between the gauze and plate and u the mobility of the ions, some of the ions coming from the gauze will be captured by the plate before the reversal of the field. For fields less than this value the plate will receive no charge. If the current to the plate is plotted against the voltage and if there is only one kind of ion present, a smooth curve should be obtained. This curve should intersect the voltage axis sharply at the critical voltage, and from the value of this the mobility of the ion can be readily determined. If there is more than one kind of ion present, the slope of the curve will increase sharply at the critical voltage peculiar to each type of ion.

As the apparatus employed has varied somewhat from time to time, it is proposed to describe the particular form with which the results given later in this paper were obtained. The modifications adopted in other work will then be indicated. The essentials are shown in Fig. 1.

The plate which receives the ions was mounted as follows. A thick brass plate, 13 cm in diameter was securely screwed on to an ebonite plate of the same size and 1.3 cm thick. The face of the plate was then turned flat in the lathe and a circular cut less than 1 mm in width was made separating an inner circular plate 8 cm in diameter from a guard-ring, which was thus a little less than 2.5 cm wide. The plate system was supported by a stout brass rod passing through an ebonite plug in the iron plate which formed the base of the apparatus. This rod served as a connection between the insulated plate and the electrometer. The guard-ring was connected to the iron plate and thus to earth. The gauze, 8 cm in diameter, was fitted to a brass ring of the same dimensions as the guard-ring. The gauze was made of brass wire .35mm in diameter and had approximately 50 meshes per cm^2. Great care was taken in soldering the gauze to the brass ring to make it quite taut so that no sagging could occur. It was necessary to insure that the lower surface of the gauze was flush with the ring. A flat circular plate was prepared slightly less than

8 cm in diameter and of a thickness equal to the difference between the thickness of the ring and of the gauze. This plate was placed against the gauze on the upper side and the whole clamped firmly in a vise over night. In consequence of these precautions, the under surface of the gauze was quite level, and its distance from the plate was given very accurately by the height of the three ebonite pillars supporting its rim. The pillars were carefully turned in the lathe. Their diameter was 1.1 cm and their

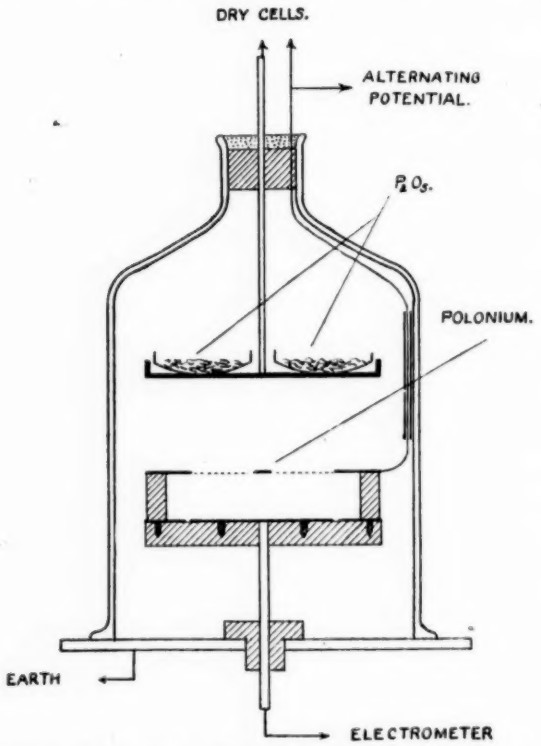


Fig. 1. Apparatus for determining mobilities by the Rutherford-Franck method.

mean height 2.494 cm, the three differing only slightly in the last figure. The pillars stood at the outer edge of the guard-ring, and a minute trace of seccotine was used to fasten them in position. The rim of the gauze rested on them without any adhesive.

The source of ionization was a deposit of polonium on the central portion of a small disk of bismuth which rested on the centre of the gauze. At a distance of 5 cm above the gauze was a parallel plate and between this and the gauze a steady potential difference was maintained by means of dry cells. In most of the work to be described subsequently, the value of this potential difference was 50 volts. The plate was fitted with a small

rim and was used to support porcelain dishes containing phosphorus pentoxide when drying was desired. The plate was supported by a rod passing out through an ebonite plug which served as a stopper in the glass bell-jar which surrounded the apparatus. A wire making connection with the gauze was brought out through the same plug. Part of the wire inside the vessel was surrounded by a thin glass tube. The bell-jar was 16.5 cm in diameter internally. It was ground on to the iron base-plate, the contact being made air-tight by the use of a little vaseline. The ebonite plug in the neck of the bell-jar was sunk about $\frac{1}{2}$ cm and the space flooded with molten paraffin wax.

The alternating potential was derived from the secondary of a transformer, one terminal of the secondary being earthed and the other connected to the gauze through a 2-volt cell. The cell was so connected that the upward field on the ions was slightly greater than the downward, so that ions which had just escaped capture at the plate were discharged by the gauze, or at least compelled to traverse the full upward distance before the next alternation of the field. The primary of the transformer was connected to the Dublin supply, the frequency of which is about 52 The voltage of the secondary, which could be readily varied by varying the resistance in the primary, was read off directly on an Ayrton and Mather electrostatic voltmeter. Two of these were used; one having the range 80-250 volts could be read accurately to $\frac{1}{2}$ volt, the other having the range 200-600 volts could be read accurately to 1 volt. The frequency was measured at the beginning and end of each set of observations and was remarkably steady. The electrometer used was of the Dolezalek type with quartz insulation and a phosphor-bronze suspension. Its sensitivity was about 1000 mm/volt and the capacity of the electrometer and apparatus was 165 cm.

Variations in Apparatus

Gauze. A number of sets of observations were made with a perforated brass plate substituted for the gauze. The plate was quite flat, 1 mm in thickness and had 12 circular holes per cm^2, each 2.35 mm in diameter. The results did not differ in general character from those obtained with the gauze except that the currents to the lower plate were considerably smaller. It is evident that a smaller number of ions found their way through the perforated plate.

Vessel. In about half of the observations a metal enclosure was used instead of the glass bell-jar. The dimensions were almost exactly the same except that the top was flat. In this case the connection to the gauze was brought out through the iron base-plate. As will be seen later, the essential character of the results was not affected by these modifications.

Apparatus for hydrogen. The apparatus used for observations on hydrogen,[2] which was also used for some work on air, differed from that described only in dimensions. The electrometer-plate was 10 cm in diameter and the guard-ring 15 cm. The height of the pillars was exactly 4 cm. The apparatus was enclosed in a brass vessel 20 cm in internal diameter.

Conditions for Accurate Observations

Constancy of ionization. This is secured by the use of polonium. From some points of view, ions produced photo-electrically are preferable, since any uncertainty as to conditions at the grid is avoided. On the other hand, one is limited to negative ions, and, a more serious matter, steadiness of ionization is difficult to attain.

Constancy of alternating field in amplitude and frequency. This is most likely to be attained from a large a.c. system such as that of the Dublin public supply. Except at certain hours of the day, the voltage as recorded by the voltmeters was remarkably steady. The practice was adopted of working during intervals in which previous experience had shown that the voltage was undisturbed. As far as may be judged from the voltmeter readings, the voltage on favorable occasions was steady to at least $\frac{1}{2}$ per cent. The curves obtained bear out this view. The maximum change of frequency noted from day to day was of the order of 1 per cent; the maximum variation between the beginning and end of an experiment was about 2 parts in 500.

Parallelism of gauze and plate. The distance between the gauze and the plate enters into the formula for the determination of mobility in the second power. It is obviously of great importance that exact parallelism should be secured. The apparatus used by the author has been specially designed in order to make sure of this point. In the form of apparatus used by Loeb, strict parallelism is very difficult to obtain. Loeb estimates an uncertainty in his mobility values of ± 3 per cent on this account.

Uniformity of field. The guard-ring should effectively eliminate any distortion of the field due to the walls of the vessel. The fact that the substitution of metal for glass made no difference in the results shows that the protection is effective. It readily appears from calculation that the density of ionization used will not appreciably disturb the field. There remains the possibility which has been suggested[5] of penetration of fields through the gauze. If the lines of force from the upper (accelerating field) penetrate through the gauze in any numbers, one would except to find a current to the lower plate when the gauze is at earth. An effect of this

[5] Miss Zimmerschied, Phys. Rev. **21**, 721 (1923)

character has been noted previously[3] and a different explanation suggested. This effect appeared only when the intensity of ionization was high and when the gas was very dry. It has not been observed in the course of the work dealt with in this paper.

Induction effects due to the alternating field. Various devices are employed by different workers in order to eliminate this cause of disturbance to the electrometer system. The simplest method is to disconnect the electrometer from earth *before* closing the primary circuit of the alternating system. The inductive effect is then almost negligible and the electrometer needle soon takes up its uniform rate of motion.

Insulation. It is essential that the insulation of the electrometer system should be good. The test of insulation applied was that the electrometer and plate should not leak more than 5 divisions per minute when charged to .14 volt, no condenser being in parallel.

Results of Experiments

In Fig. 2 are plotted some of the current-voltage curves obtained with negative ions. Curve A is the result of some observations made on air saturated with water-vapor. The lower part of the curve was obtained with a condenser of capacity .001 mf in parallel with the electrometer, the upper part with a capacity of .003 mf. The readings with the higher capacity were multiplied by the appropriate factor to make them correspond to the readings with the lower capacity. The two sets of observations overlap between 470 and 490 volts. It is not possible with any pretence to accuracy to draw through these points a smooth curve cutting the axis sharply. A nearer approximation represents it as a number of straight lines intersecting at 520, 474 and 435 volts. The constant (mobility $\times$ critical voltage) was 710. The curve therefore represents ions of mobilities 1.36, 1.50 and 1.63, corresponding to three of the ions to which the author attributes the bulk of the ionization in moist air. The curve shows the presence of another ion, but the intercept with the voltage axis is not sharp enough to allow of its mobility being calculated. Now it is not contended that the curve given is a simple composite of four curves, one for each kind of ion. It will be seen later that close examination would show it to be more complex. But it does show that the bulk of the ions in moist air tend, as has been claimed in previous papers, to fall into four principal groups of which three are here indicated.

A remarkable confirmation of this result has been found in the cloud experiments of C. T. R. Wilson.[6] In one photograph, the separation in an electric field of the four kinds of ion produced in the track of an α-

[6] C. T. R. Wilson, Proc. Camb. Phil. Soc. **21**, 405 (1923)

particle is shown by four parallel cloud-tracks. It is difficult to conceive of any possible explanation of this photograph other than the four-fold character of the ionization.

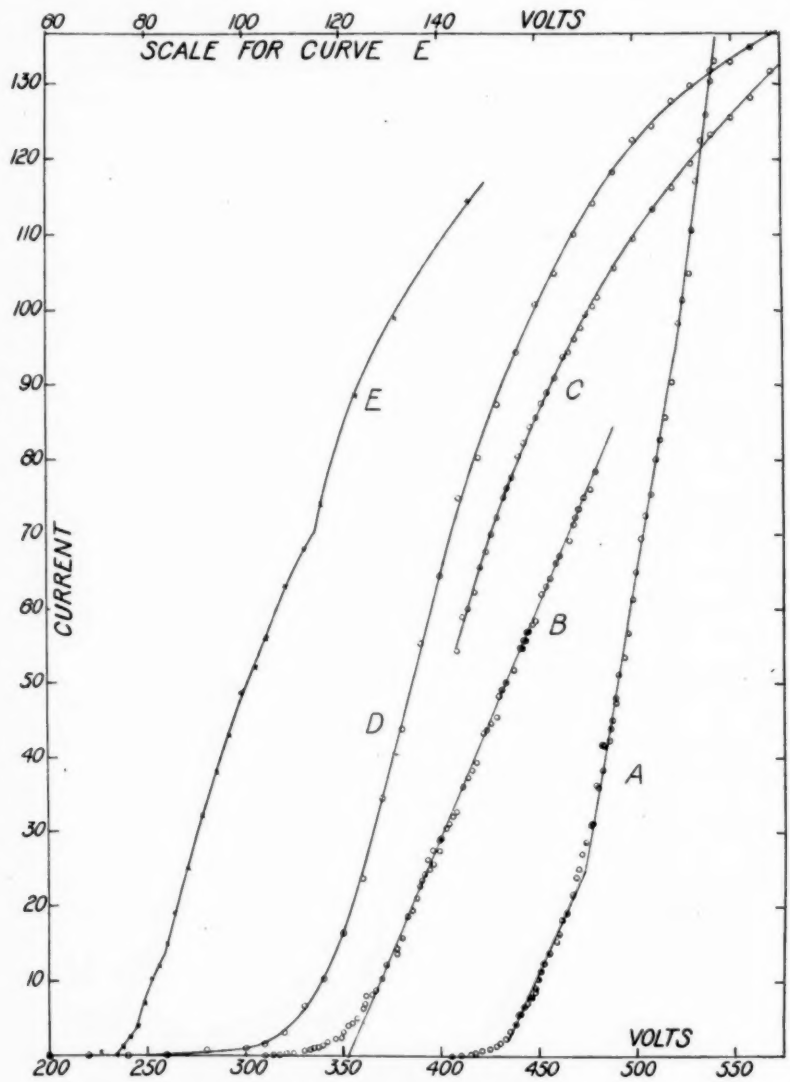


Fig. 2. Current-voltage curves
A, saturated air; B, air partially dried; C and D, dry air; E, Loeb's curve.

In the work described in the present paper, the interest was not so much in the ionization in moist air as in the changes produced by drying and the accurate estimation of the mobilities of the faster groups of ions.

Porcelain dishes containing phosphorus pentoxide were inserted and the vessel was sealed up. Two days after the drying began Curve B was obtained. The upper part of this curve was taken with a capacity of .008 mf in parallel with the electrometer, the lower parts with .003 and .001 mf. The overlapping parts agree very well except for some observations between 390 and 400 volts. The ordinates of this curve (and of Curves C and D) should be multiplied by 2.67 for comparison with Curve A. If what Loeb calls the "asymptotic foot" at the bottom of the curve be disregarded, a straight line may be drawn through the plotted points. This line intersects the voltage axis at 352, and it might be said that the observations therefore indicate the existence of a single ion of mobility $710/352 = 2.02$. But in the opinion of the writer, this summary treatment does not reveal the true conditions. In the first place the asymptotic feet in these curves cannot be so lightly disregarded; and in the second place, the straight-line part of the curve will, if attentively examined, show a remarkable peculiarity. It has a gapped appearance due to the fact that while the observed voltages are fairly uniformly distributed, the current values show sudden jumps at regular intervals. In the spaces between the gaps, the current values, while never very far from the straight line, exhibit a tendency to lie first above and then below it. In fact it would seem that the curve is not a straight line but a series of short curves, each short curve corresponding to a step of about 10 volts. It might be alleged that this appearance is quite illusory; that the regularly occurring curvature is due to some experimental error—some error in reading the voltmeter for example. Now it will be shown later when the curve is examined closely and not in the rather crude fashion just given, that this complex structure can be quite definitely and accurately established. On the other hand, Curve C which was obtained with very dry air, is plotted to show that at a higher degree of drying the upper part of the curve is quite smooth. If the form of Curve B is due to experimental irregularities of any kind, they should equally well affect Curve C, for the only difference is that one curve was plotted 40 days later than the other.

In order to compare the results with those obtained by Loeb, Curve D has been plotted. This curve was obtained 23 days after drying had begun, that is 21 days after Curve B. All observations were taken with a condenser of .008 mf in parallel with the electrometer. Curve E has been plotted from Loeb's observations taken from Fig. 3 of his paper. The points have been taken from an enlarged photograph of Loeb's curve and it is believed that they are accurately reproduced. While in general outline there is not much difference between the author's curve and that

of Loeb, it will be noticed that the latter is not of as regular a character. Loeb draws a smooth line through his points, but the author has ventured as the diagram shows, to follow the points rather more closely. Possibly Loeb's observations are inaccurate owing to want of steadiness in the ionization and want of parallelism is his apparatus, but as he states that each point was obtained from the average of two concordant electrometer readings, it may be assumed that inaccuracy on the first head at least has been eliminated. This being so, the author cannot find any reason for refusing to give to Loeb's experimental points their full value, especially as they can be made to lie accurately on a number of smooth curves instead of very inaccurately on one. There can be no doubt whatever that Loeb's curve shows a bend at 115 volts. It also shows but not so strikingly, bends at about 83.5 volts and 78 volts and there is a slight indication of a sag in the curve at about 103 volts. Loeb's mobility constant was 169 approximately. Therefore his curve shows quite distinctly the ion of mobility $169/115 = 1.47$, also ions of mobility 2.02 and 2.17. It shows indications of a possible ion of mobility about $169/103 = 1.64$. It is hardly necessary to point out how closely these results agree, not merely in general character, but in the actual values of the mobilities with the results published by the present writer. The curve for dry air (D) is much smoother than that of Loeb, but seems to have the "asymptotic foot" better developed. It is, in fact, what the author is accustomed to regard as the characteristic curve for a dry gas, while Loeb's curve is intermediate in character between that for a dry gas and that for a saturated gas (A). In other words, the drying in Loeb's case seems to have been imperfect. The question of drying is not a simple one, but the work of Baker[7] and others seems to show that the gas in a vessel cannot be dried by simply filling it through drying materials. Prolonged contact of the gas with the drying agent is necessary.

Loeb's other curves (Figs. 1 and 2 of his paper) are not so well suited for comparison, principally because they show too small a number of points over the range under discussion. Inside that range, however, they certainly show irregularities of such a character as to suggest that if more points were determined the complex character of the curves would be disclosed.

The Curves A to D have been plotted only to show that there is no divergence between the author's results and those of Loeb so far as the latter has gone, and that it is not necessary to seek for explanations of differences which have not been proved to exist. Curves of this char-

[7] Baker, Jour. Chem. Soc. (London) **81**, 400 (1902); **101**, 2339, (1912); **121**, 568 (1922)

acter have been regarded by the author as only in the nature of preliminary surveys of the ground. The real investigation consists in the close scrutiny of the current-voltage curve stage by stage.

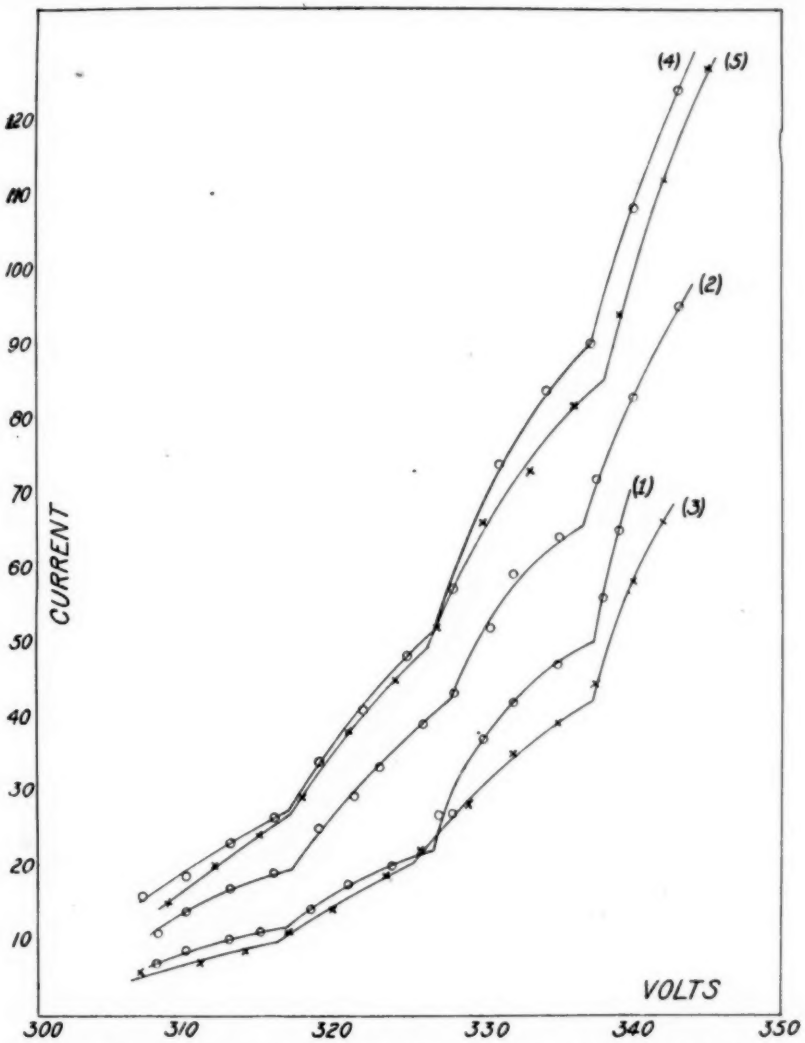


Fig. 3. Current-voltage curves for 300-350 volts, at different stages of drying.

Accurate Investigation of the Structure of Current-Voltage Curves

In Fig. 3 a number of curves are plotted showing the examination of the current-voltage curve over the range 310-345 volts, that is, corresponding to the rounded portion at the foot of Curve D. Curve 1 was

plotted two days after drying had begun, that is on the same day as Curve B. The currents over that range of voltage were then small so that no auxiliary capacity was used. Curves 2 and 3 were plotted after 16 and 25 days drying respectively. Here and also in the case of Curves 4 and 5, a condenser of .001 mf was used in parallel with the electrometer. For purposes of comparison with the other curves, the ordinates of Curve 1 should therefore be divided by $6\frac{1}{2}$. While the effect of drying as shown by Curve 2 has been to produce a big increase in the current values, this increase had not been maintained in Curve 3—in fact there is a considerable reduction. From this and other evidence it was concluded that drying was not going on at a satisfactory rate; certainly not as rapidly as in previous experiments.[3] It was thought possible that the difference was to be attributed to the glass vessel as metal only had been used in the previous work in which a high degree of drying was shown by the rapid appearance of ions of high mobility. The problem is perhaps not so much to dry the gas as to dry the walls of the vessel. A metal vessel was therefore substituted for the glass bell-jar, fresh P_2O_5 was introduced and the apparatus sealed up once more. Curves 4 and 5 were obtained with the new apparatus 31 and 39 days later. These curves, which are very nearly identical, show a considerable increase in current values over those obtained with the first apparatus, but even in this case it is believed that a really high degree of drying was not reached. It is probable that there were minute leaks in the apparatus and that moist air from outside found its way in.

The curves which have been reproduced in Fig. 3 are selected curves only in the sense that curves have been picked which cover the whole range. Every electrometer observation has been plotted. These curves as well as the much greater number which have not been given, agree in showing that the current-voltage curve is made up of a number of curves, convex upwards, showing intersections at 317, 327 and 337.5 volts. In the absence of any explanation of how a periodic character could be impressed upon the curve by any property of the field, of the grid or of the recording instruments, there is no escape from the conclusion that each intersection represents a distinct group of ions.

In Fig. 4 are given six curves covering the range 340-385 volts. As before, these curves represent different stages of drying, the lowest curve having been plotted 1 day after drying began. All curves are plotted to the same scale. Only one of these curves (the short curve on the left-hand side) was obtained with the apparatus in the metal enclosure. All curves agree in showing discontinuities at 348, 358.5, 368.5, and 378.5 volts. It is

hardly necessary to point out that if only a few widely spaced observations are taken, the true nature of the curve will not be disclosed.

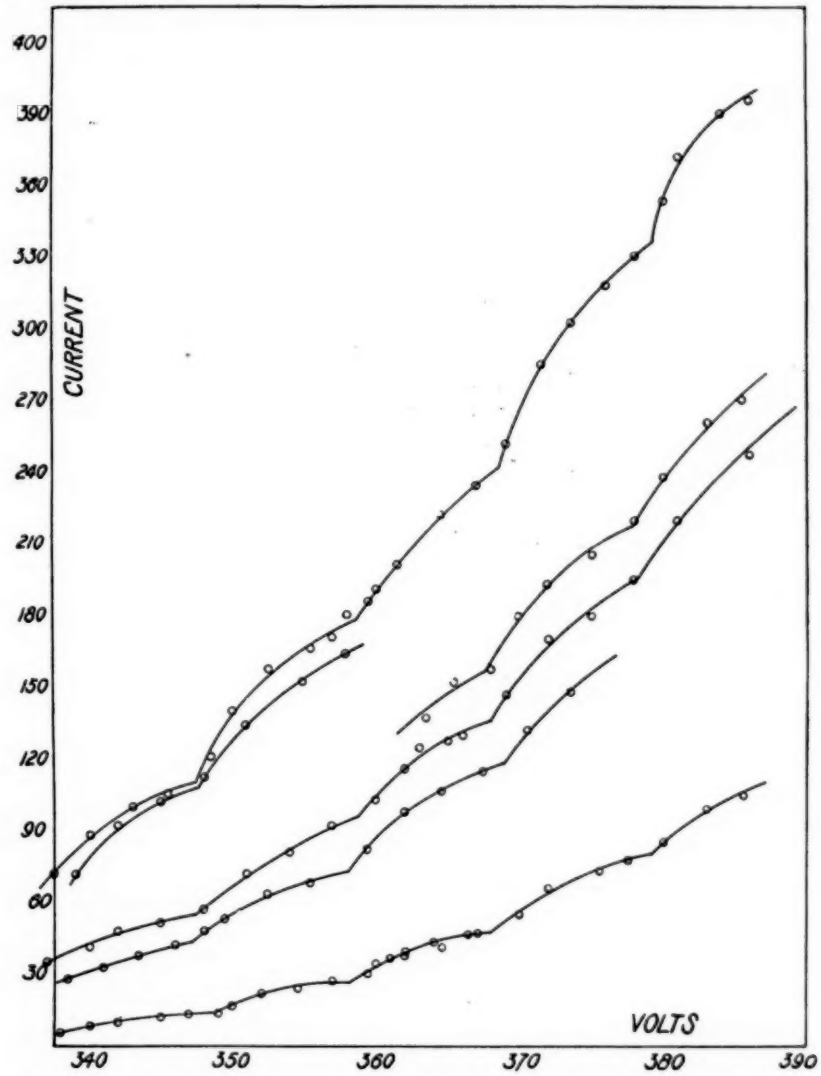


Fig. 4. Current-voltage curves for 340-390 volts, at different stages of drying.

From the accurately established critical voltages the following mobility values are deduced:

Critical Voltage	Mobility
317	2.24
327	2.17
337.5	2.10
348	2.04
358.5	1.98
368.5	1.93
378.5	1.87

It is not proposed in the present paper to deal in detail with the examination of the curves for higher or lower mobilities than those just given. The values for the mobilities of the faster ions are not yet all definitely known, and what is perhaps more important, the number of groups intervening between the fastest given above (2.24) and the ion of mobility about 12 (which the author regards as the mono-molecular ion) is still slightly uncertain. Judging from the best and most recent experiments, the first three ions have mobilities about 11.5, 7.5 and 6 and there appear to be ten or eleven other ions intervening between these and the fastest ion given in the table. As regards the slower ions there is ample evidence. Curve B has already shown that there is an inflection for about every 10 volts between 250 and 470 volts. Thus the list above can be continued giving critical voltages at about 390, 400 etc. to 470 volts. This is amply confirmed by observations taken over this range with both positive and negative ions. Accurate observations show that the critical voltages should be approximately 388, 398, 408 etc. and that this succession continues up to 528 volts and beyond it. Of course, if the air is very dry, Curve C shows that the slower groups do not appear.

The author interprets these results in terms of a theory of the constitution of the ion put forward by him some years ago.[8] According to this theory the ion is a cluster of water molecules containing any number of molecules up to 30 or 40. Any size of cluster may be present depending on the conditions; for example in moist air four types are generally found. Drying tends, especially in the case of the negative ion, to eliminate the larger clusters and to bring the smaller ones into prominence. In the original paper the author suggested that the four kinds of ion ordinarily prominent in moist gases contained 18, 24, 30 and 36 molecules of water respectively. The mobility of these four hypothetical ions was calculated using a formula due to Sir J. J. Thomson. The value found for the mobility of the ion composed of 30 water-molecules was 1.53. This ion is usually very prominent; Loeb's Curve E shows it having mobility 1.47 and Curve A shows it having saturation voltage 474 and mobility 1.50. The close analysis of the curves shows that the correct saturation voltage should be 468 (mob. = 1.52). If our view as to the constitution of the ions is correct, the next slower ion—critical voltage 478—has 31 molecules of water, the next 32 and so on. If we continue in this fashion we find that the ion of 36 water-molecules should be disclosed at critical voltage 528. This is a notably prominent ion in all curves taken with moist air. Its mobility is 1.34, which corresponds with the calculated value 1.31. Its

[8] J. J. Nolan, Proc. Roy. Soc. **94**, 112 (1917)

prominence is shown by Curve A, which gives its mobility as 1.36. On the other hand, going from the ion of 30 water-molecules to the smaller ions, we find that the ion indicated by the critical voltage 408 should have 24 water-molecules. Critical voltage 408 gives mobility 1.73; the mobility calculated by the author for an ion of 24 water-molecules is 1.72. Continuing in the same way, the ion indicated by the critical voltage 348 should have 18 water-molecules. Mobility determined (see table) = 2.04; mobility calculated = 1.97. The fastest ion in the table should have 15 water-molecules; the value calculated is 2.17, the value found is 2.24. There should then be 14 possible ions left; it has been already stated that that number, or possibly one less than it, have been found.

The numbers (18, 24, 30 and 36) originally suggested for the more prominent ions were chosen because they fitted the results of experiment better than any others. "With fuller information the ions might be better represented in terms of some other unit rather than six."[8] There would now seem to be considerable justification for believing that the numbers originally suggested cannot be far wrong. Apart from the evidence just given, the work on gaseous hydrates[9] which shows that bodies of the type $M(H_2O)_6$ are readily formed, even when M is a molecule of such a gas as argon, is highly significant in this connection.

Discussion

The author has in previous papers shown by various methods that the ions in moist air fall into four distinct groups. Direct confirmation of this has been found in the work of C. T. R. Wilson. It is now possible by refined observation to follow the building up of the ions constituting these groups and to detect the less prominent intermediate stages. The number of intermediate stages found is in accordance with the number of molecules previously assigned to each ion. The smaller ions, when brought into prominence by extreme drying, afford further confirmation by their absolute mobility values and by their spacing. For many reasons it is believed that the unit out of which the ions are built is the water-molecule.

Apart from the evidence brought forward in this paper, the theory which regards the ordinary ion as a charged gas-molecule is quite untenable. When the author originally found[1] an ion of mobility 12.5 in the air ionized by the decay products of radium, he was unaware of the results of Franck,[10] Altberg[11] and Moore.[12] Franck found a negative ion

[9] See Bouzat, C. R. **176**, 253 (1923), and de Focrand, C. R. **176**, 355, (1923)
[10] Franck, Ann. der Physik **21**, 972, (1906)
[11] Altberg, Ann. der Physik **37**, 849 (1912)
[12] Moore, Phys. Rev. **34**, 81, (1912)

with a mobility of 12.26 in dry air; Altberg found a negative ion of mobility 10.1 and Moore found a negative ion of mobility 9.72. The agreement is good considering the great differences in the methods employed by these workers. That this is the true monomolecular ion can hardly be doubted. The values found for the fastest positive ions by these workers are respectively 3.22, 7.5 and 6.43. Again, the present writer can find no reason for refusing full credit to the results of Haines[13] on hydrogen; his own observations confirm those of Haines and he has recently in dry hydrogen found Haines's ion of mobility 40.6. Finally, the fact that the recoil atom has about the same mobility as the ordinary positive ion is fatal to the "small-ion" view, unless a form of theory is invoked which would make the mobility independent of the mass. Even this very questionable alternative is ruled out by the observations of C. T. R. Wilson[6] who has obtained photographs showing definitely that the atom of ThA was displaced twice as far by an electric field as the ordinary ions in the same time. The fact that a body of mass 216 can move twice as fast as the ion under an electric field, shows not only that the ion is a cluster, but that it is a cluster containing a considerable number of molecules.

The author is indebted to Mr. P. B. Carolan from whose observations the curves in this paper were plotted. It is hoped to publish the results of Mr. Carolan's observations more fully on a subsequent occasion, especially those dealing with ions of high mobility which have been only lightly touched upon in this paper.

UNIVERSITY COLLEGE, DUBLIN.
December 8, 1923.

[13] Haines, Phil. Mag. **30**, 503, (1915) and **31**, 339, (1916)

A METHOD OF PRODUCING A SQUARE WAVE OF RADIO FREQUENCY

By J. L. Bowman

Abstract

A radio-frequency square wave, *suitable for the measurement of the mobility of ions*, has been obtained by using a circuit containing three vacuum tubes. The first tube operates as an oscillator. The potential of the second tube, which operates as a rectifier, is controlled by the grid circuit coil of the oscillator. The third tube is connected so that the plate current will be cut off during the half period when the rectified current is flowing in the plate circuit of tube 2. The rise of the voltage of the square wave is approximately exponential, due to the charge on the grid and the plate of tubes 2 and 3, which must be discharged through a resistance which couples the plate circuit of tube 2 to the grid of tube 3. A cathode ray oscillograph tube indicates that the voltage rises to approximately its maximum value in 1/10 of the half period. A square wave of 120 volts may be obtained with Western Electric "E" tubes. Three methods of amplification are given by which a square wave with a very much larger voltage may be obtained.

Introduction

THE apparatus for producing a square wave of radio-frequency has been designed because of the application it has in the measurement of the mobility of ions. The investigations have been confined to vacuum tube methods. The circuits found to be most satisfactory are shown in Fig. 1. Tube 1 operates as an oscillator, so arranged that the mutual

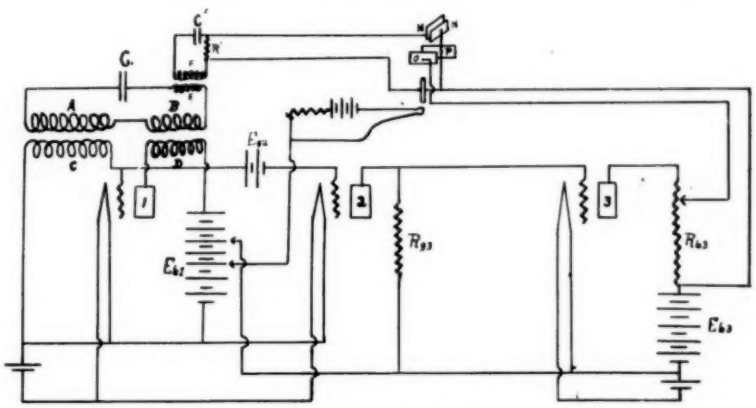


Fig. 1. Diagram of circuit.

inductance of the coils *A*, *B*, *C*, *D*, may be varied. Tube 2 may be regarded as a rectifier and the circuits immediately associated with tube 3 produce the square wave.

Method of Operation

The method of operation is as follows. The oscillator imposes an alternating e.m.f. on the grid of tube 2. A certain constant negative potential is placed on the grid by the battery E_{g2} such that during almost one-half of the period the alternating e.m.f. causes the plate current to be cut off. Variations of the plate current impose an alternating e.m.f. on the grid of tube 3. During the time there is no current through R_{g3}, the grid of tube 3 is zero with respect to its filament, and a constant current will flow through R_{b3}, but during the other half period there will be a large negative potential imposed on the grid of tube 3, thus cutting off the plate current. Tubes 2 and 3 must work below the characteristic curve during a part of the period. The square wave thus consists of a sudden rise to a constant voltage and a rapid decrease to zero voltage.

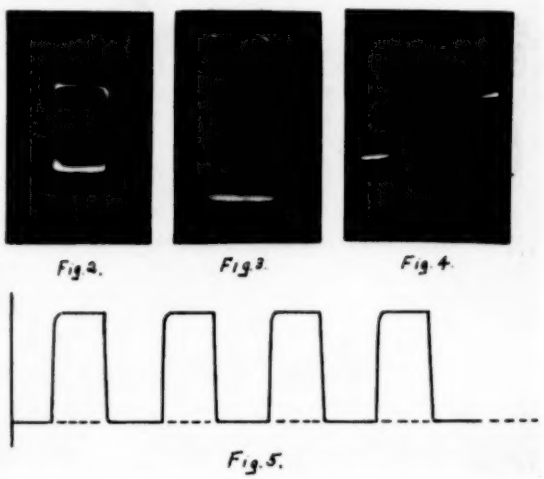
The wave will be very nearly a perfect square if the e.m.f. imposed on the grid of tube 2 is large. This end may be secured without injury to the tube by arranging the circuits as shown in Fig. 1. The grid of tube 2 connects to the grid of tube 1, the potential of which is controlled by the alternating e.m.f. across the grid circuit coil of the oscillator. During the negative half period the grid of tube 2 will reach a very low negative potential, but during the positive half period the rise will be very rapid to about 15 volts, when a current from grid 1 and grid 2 opposes the increase. Therefore the positive half cycle does not increase the grid abnormally. This half cycle, having been amplified and inverted, is imposed on the grid of tube 3. The result is that a square wave of large voltage may be obtained without using an amplifier.

The Form of the Square Wave

The form of the square wave was observed by applying a part of the voltage of the square wave to one pair of plates (O, P) of a Western Electric cathode ray oscillograph tube (Fig. 1) and by connecting the other pair of plates (M, N) to the ends of a resistance in series with a variable condenser and an inductance, which is inductively coupled to the oscillation circuit of tube 1. By proper adjustment of the resistance R', the capacity C' and the mutual induction of coils E and F, the e.m.f. imposed on one pair of plates of the oscillograph tube will be about 90° out of phase with the e.m.f. of the other plates. The sine wave imposed on plates M and N produces a straight line on the oscillograph and the square wave produces a straight line at right angles to it. When the difference of phase is about 90° the voltage changes of the square wave take place when the e.m.f. of the sine wave is very near a maximum or a minimum. Thus the electron beam may be deflected to the right by the

sine wave, then vertically upward by the square wave then to the left by the sine wave and then vertically downward by the square wave, the entire curve being traced once each period. The photographs of the screen of the oscillograph show the form of the curves thus obtained. Fig. 2 represents 60 volts and Fig. 3 represents 120 volts.

The vertical lines in the photograph are quite indistinct, indicating that the rise and fall of the voltage of the square wave is very rapid. The deflection along the horizontal lines represents a simple harmonic movement of the electron beam, so that the voltage of the square wave changes near the time when the rate of the horizontal deflection is slowest. Therefore the curve obtained in this manner does not represent the exact shape of the square wave which would be obtained by plotting the voltage against the time t.



Figs. 2-5. Oscillograph records.

If R' and C' are removed from the circuit and the plates M, N are connected directly to the ends of the coil F, the sine wave voltage and the square wave voltage will be in phase, and the vertical deflections will take place while the horizontal deflections are most rapid. The curve obtained in this manner is shown in Fig. 4. By measuring the horizontal displacement which takes place while the beam is being displaced vertically, the time of rise of the voltage of the square wave was found to be about 1/10 of the half period and the time of fall is about 2/3 of the time of rise. From these observations approximate calculations may be made of the form of the square wave which is represented in Fig. 5.

The form of the square wave depends (1) on the amplitude of the wave imposed on the grid of tube 2; (2) on the capacities of the various circuits and (3) on the voltage amplification factor of tube 2. Using Western Electric "E" tubes, with circuit constants to be given later, the time required for the original wave to vary over a range sufficient to produce the square wave was about 1/20 of the period of oscillation.

The rate of rise of the voltage of the square wave decreases as the capacity of the circuits and tubes is increased. Due to these capacities the voltage changes will be approximately exponential, as the charge on the plate and the grid is being discharged through the external resistance of the plate circuit. The voltage will increase rapidly at first, but as the grid potential approaches a limiting value the rate of increase gradually becomes less. A slight bend showing this effect can be observed in the photographs of the curve (Figs. 2 and 3). As the voltage of the square wave decreases, the grid of tube 3 reaches its limiting potential after the current in the plate circuit has been cut off. This eliminates a part of the capacity effect, so that the time of fall will be less than the time of rise of the voltage.

The capacity in series with R_{g3} consists of the capacity of the plate and the filament and of the plate and the grid of tube 2 and the capacity of the grid and the filament and of the grid and the plate of tube 3. As the grid varies in potential the plate also varies but with the opposite potential, so that the total discharge through R_{g3} is of such magnitude that the square wave will be appreciably distorted if R_{g3} should be more than 2000 ohms when E_{b3} is 200 volts, but for higher plate voltages it has been found empirically that R_{g3} may be approximately equal to $(R_{b3}+R_0)/\mu_0$ in which R_0 is the internal impedance of the tube and μ_0 is the amplification constant. The amplification factor μ of tube 2 will be small, as can easily be observed by plotting the voltage across R_{b3} against the grid voltage, or it may be obtained approximately from the relation $\mu=\mu_0 R/(R+R_0)$.[1] The rate of rise of the voltage of the square wave, due to an increase of the amplification factor, is opposed by the capacity effects of the tube, thus requiring proper adjustment of R_{g3} to obtain the best wave form.

Condition for Best Operation

If we desire to produce a square wave for any assigned purpose it is necessary to determine (1) the voltage which is to be obtained from the square wave; (2) the current that can be taken off without too great

[1] Van Der Bijl, Proc. Inst. Radio Eng. **7**, 97 (1919)

change of voltage; and (3) the resistance which can be used in the circuit to which the apparatus is coupled so that the added capacities will not distort the wave form. In order to keep the resistance small the impedance of the tubes should be small. The best operation is found by making R_{b3} about equal to the impedance of the tube. The voltage of the square wave obtainable will then be about 1/2 of E_{b3}. It may be increased to 2/3 of E_{b3} by increasing the resistance R_{b3}. Or it may be increased by making E_{g3} positive, say 10 volts or even more as a grid current through R_{g3} causes no appreciable disturbance. The tube may even be operated up to the saturation point of the curve, which is quite low when the resistance R_{b3} is large. The actual square wave voltage thus obtained with "E" tubes, was 200 volts by using 375 volts on the plate. The voltage E_{b3} may be increased above its normal operating value, since there is a large resistance in the grid circuit and because the plate current is flowing only half-one of the time and when it is flowing the voltage between the plate and the filament is decreased to $(E_b - RI)$.

After choosing proper values for E_{b3} and R_{b3}, R_{g3} should be approximately equal to $(R_{b3}+R_0)/\mu_0$ but it is better to use a variable resistance and to adjust it to its maximum value while observing the shape of the wave. Tube 1 operates best when E_{b1} is about 180 volts, and tube 2 operates successfully with a plate voltage of 140 volts. Plate batteries are shown in Fig. 1 for simplicity, but they may all be replaced by one d.c. generator of 400 or 500 volts. This can be done by placing a large resistance in the generator circuit and joining the negative end of the resistance to the filament of tube 1 and tapping off the desired voltages to the plates of tubes 1 and 2. The point at which the circuit from the plate of tube 2 connects to the resistance in the generator circuit is directly connected to the filament of tube 3, so that the desired plate voltage for tube 3 may be obtained by tapping off at a point of higher potential. If an oscillograph tube is used to observe the wave form, the generator may also be used to place a suitable potential on the anode similar to the connections shown in Fig. 1. The adjustment so that each half period of the wave is equal, is made by varying the voltage on the battery E_{g2}, which should be about 20 volts negative. The oscillator should produce a voltage across the condenser of about 450 volts. The frequency used was about 100,000 but the wave form is almost as good up to 600,000, which is as high as trials were made.

The resistance should be as non-inductive as possible, though ordinary resistance boxes are quite successful. Very good results were obtained by using resistances made of quartz fiber sputtered with platinum and

mounted in oil.[2] It is essential that capacities in all circuits be made as small as possible. If the connections are made as shown in Fig. 1, the capacity effects between the batteries will be largely eliminated. If the batteries are replaced by a generator, a condenser should be placed in parallel with each part of the resistance of the generator circuit which is placed in a plate circuit.

Methods of Amplification

If a square wave having an e.m.f. of more than 150 volts is desired, amplification may be obtained by either of the three following methods. The voltage of the rectified wave of tube 2 may be increased by placing another tube in parallel with it, making it possible to increase the voltage

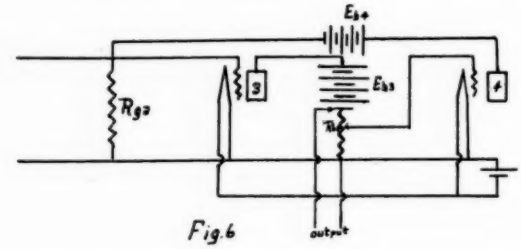


Fig. 6

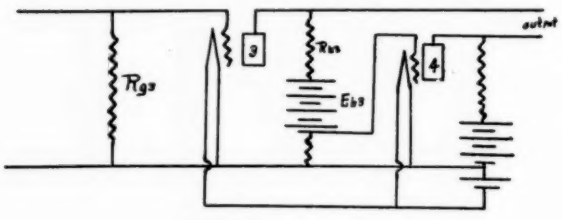


Fig. 7

Figs. 6-7. Circuits used for amplification.

on the plate of tube 3. Another method (Fig. 6) is to place the extra tube so that the grid is operated from a part of the voltage across R_{b3}, and to connect the plate in series with R_{g3}. In this way the negative range of potential of the grid of tube 3 is greatly increased, since the current in the plate circuit of tube 4 is added to the current of the plate circuit of tube 2. In fact the amount of current fed back into the grid circuit of tube 3 can easily be adjusted so that a very small range of the original wave imposed on the grid of tube 3 is necessary to produce a square wave of good form. This method will be very useful if for any reason the amplitude of the original wave is small. The voltage of E_{b1} should be

[2] Frayne, Phys. Rev. **21**, 348 (1923)

about 1/2 of E_{b3}. Another method of amplification is to add another tube (Fig. 7) to be operated similarly to tube 3 by imposing a part of the voltage across R_{b3} on the grid of tube 4. The total voltage obtained by this method, when R_{b3} and R_{b4} are placed in series in the circuit in which the square wave is to be used, will be the sum of the voltages across R_{b3} and R_{b4}. If this method is combined with the first method of amplification given, a very large voltage may be obtained.

In conclusion I wish to express my thanks to Prof. W. F. G. Swann for suggesting the problem and for the valuable assistance he has given. I also wish to thank Dr. F. M. Kannenstine for the suggestions he has offered. The investigation has been made possible by the courtesy of Dr. E. H. Colpitts of the Western Electric Co., who loaned the tubes which were used in the experiments.

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THE THEORY OF THERMIONICS

By H. A. Wilson

Abstract

Thermodynamical theory of electron emission from metals.—By means of a reversible cycle similar to that first used by O. W. Richardson, an accurate expression for the thermionic emission is obtained and it is shown that the constant in the equation for the vapor pressure of the electrons is equal to the chemical constant for electron gas. It is shown that if all the internal heat of evaporation of the electrons is due to electrical forces then Richardson's original equation $I = A\theta^{1/2}\epsilon^{-b/\theta}$ must be correct and the specific heat of the negative electricity in the metal must be the same as for a monatomic gas at constant volume, but that if this specific heat is small, as is known to be the case, then all the internal heat of evaporation cannot be due to electrical forces and Richardson's second equation $I = A\theta^2\epsilon^{-b/\theta}$ is a better first approximation to the exact relation. It is shown that the equation $L = R\theta_2 d(\log p)/d\theta$ where L is the heat of evaporation of a liquid at pressure p and temperature θ is not exactly true for the evaporation of electrons. It is pointed out that the thermodynamical theory of evaporation was applied to electron emission by the writer in 1903 and that O. W. Richardson in 1912, M. V. Laue in 1918, R. C. Tolman in 1921 and S. Dushman in 1923 have made further applications of it to the same question.

Quantum theory of the chemical constant.—A simple way of calculating the size of the region element in the state space for a monatomic gas is given which makes it equal to Nh^3 where N is the number of molecules in the gas and h Planck's constant. This gives the same expression for the chemical constant as that found by Sackur.

THE term thermionics was introduced by O. W. Richardson to denote the branch of physics dealing with the emission of electrons by metals at high temperatures. Richardson's kinetic theory of the emission appeared in 1901.

The emission of electrons by hot bodies is a kind of evaporation and the thermodynamical theory of evaporation was applied by the writer[1] in 1903 to calculate the variation of the emission with the temperature. The electrons were supposed to behave like a perfect gas which could be in equilibrium with the metal at a pressure p and the latent heat of evaporation L of one mol was taken to be given by the well known equation*

$$L = R\theta^2 \frac{d(\log p)}{d\theta}$$

[1] H. A. Wilson, Phil. Trans. A **202**, 243 (1903)

* It is shown in the present paper that this equation is not exactly true for electron gas evaporating from a metal.

where R is the gas constant for one mol and θ the absolute temperature. Integration of this equation gave p in terms of θ and the emission per cm^2 per sec. was obtained from p by supposing that the kinetic theory of a perfect gas could be applied to the electron gas and that the number of electrons emitted was equal to the number striking unit area in the gas at pressure p. The internal heat of evaporation P was supposed to be given by $L=P+R\theta$ and P was supposed to vary with the temperature so that $P=P_0+a\theta$, where a is a constant. The pressure p was then given by

$$\log p=-\frac{P_0}{R\theta}+\left(\frac{a}{R}+1\right)\log\theta+\text{constant}$$

and the thermionic current I by

$$I=A\,\theta^{\frac{1}{2}+a/R}\epsilon^{-P_0/R\theta}$$

where A is a constant.

Richardson[2] considered a reversible cycle in which electrons were supposed to evaporate from a metal at a high temperature and to be condensed in the same metal at a lower temperature. In this way he got

$$\log p=-\frac{P}{R\theta}+\frac{5}{2}\log\theta+\int\frac{S\,d\theta}{R\theta}+\text{constant}$$

where S is the heat capacity of the electricity in the metal per Faraday. This equation, if we take S to be constant, shows that the constant a in the writer's equation above must be equal to $\frac{3}{2}R+S$. On Richardson's original theory we should expect to have $S=-\frac{3}{2}R$ so that $a=0$ and

$$\log p=-\frac{P_0}{R\theta}+\log\theta+\text{constant}$$

which gives Richardson's well known original equation

$$I=A\,\theta^{1/2}\epsilon^{-P_0/R\theta}$$

Richardson pointed out that the values of S found for different metals are all small compared with R so that it is approximately correct to put $S=0$ and using also $L=R\theta^2 d(\log p)/d\theta$ he showed that $P=P_0+\frac{3}{2}R\theta$ and

$$\log p=-\frac{P_0}{R\theta}+\frac{5}{2}\log\theta+\text{constant}$$

which gives

$$I=A\,\theta^2\epsilon^{-P_0/R\theta}.$$

Richardson definitely adopted this equation as theoretically superior to his original equation, though both represent the experimental results

[2] Richardson, Phil. Mag. **23,** 602 (1912); "Electron Theory of Matter," p. 448 Cambridge 1914; also "Emission of Electrons from Hot Bodies," p. 30, Longmans 1921.

equally well, and he proved that the constant A must have nearly the same value for all metals. Later[3] he found that this equation can be obtained by an application of the quantum theory to the problem and obtained a theoretical value for the constant A.

In a recent paper on electron emission from metals S. Dushman[4] has calculated the emission thermodynamically by assuming it analogous to evaporation and has determined the absolute value of the constant in the equation for log p by putting it equal to the chemical constant for electron gas as calculated by Sackur, Tetrode and Stern by means of Boltzmann and Planck's theory of entropy. Dushman also assumes that the heat capacity of the electrons in the metal is negligible and so gets Richardson's second equation $I = A\theta^2 \epsilon^{-P_0/R\theta}$ with $A = 2\pi mek^2/h^3$ where k is the gas constant for one molecule, m the mass and e the charge of an electron and h Planck's constant.

The assumption that the thermodynamical theory of evaporation can be applied without modification to thermionic emission requires justification and Richardson's reversible cycle supplies this up to a certain point but it is not clear that the constant in the equation for the vapor pressure of the electron gas is equal to the chemical constant for electrons. Tolman[5] has shown that the entropy of the electron gas calculated from the quantum theory of entropy agrees nearly with that calculated from the heat of evaporation, which shows that Dushman's assumption is at any rate approximately true.

The quantum theories of the chemical constant are not satisfactory. The main objects of the present paper are to attempt to show that the constant in the equation for log p is exactly equal to the chemical constant for electron gas, to give a simple method of calculating the chemical constant on the quantum theory and to obtain an accurate expression for the thermionic emission on the thermodynamical theory of it.

The analogy between the evaporation of a liquid or solid and the emission of electrons by a metal is not perfect. If any appreciable number of electrons is supposed emitted the negative charge in the gas and the positive charge on the metal become too large for their effects to be neglected. This difficulty can be overcome by using a reversible cycle in which electrons are supposed to be emitted at one temperature and simultaneously absorbed at another temperature so that the number of electrons outside the metal can be supposed constant and very small. A cycle of this kind was used by Richardson but he did not obtain the

[3] Richardson, Phil. Mag. **28**, 633 (1914)
[4] Dushman, Phys. Rev. **21**, 623, (1923)
[5] Tolman, J. Bur. Chem. Soc. **43**, 1592 (1921)

complete solution of the problem by means of it alone. The application of the first and second laws of thermodynamics to such a cycle is sufficient for the solution of the problem but the equations obtained differ from those for the evaporation of a liquid by terms containing the electrical potentials. By supposing these potentials equal to zero the equations become precisely similar to the equations for evaporation of a liquid so that the constant in the vapor pressure equation can be shown to be equal to the chemical constant for electron gas.

It will be convenient to compare two similar reversible cycles one involving the evaporation and condensation of a liquid and the other the evaporation and condensation of electrons from a metal.

Consider two vessels containing the liquid one maintained at constant temperature θ_1 and the other at θ_2 and let them be connected by a fine tube through which the liquid can flow. Let the liquid at θ_1 be in equilibrium with its vapor at pressure p_1 and let that at θ_2 be in equilibrium with its vapor at p_2. Now suppose one mol of liquid evaporated from that at θ_1 and one mol of vapor condensed in the liquid at θ_2 and let one mol of the liquid flow through the tube from θ_2 to θ_1. The heat required to maintain the temperatures constant during this operation will be $L_1-L_2+\int c d\theta(\theta_2 \text{ to } \theta_1)$ where L_1 and L_2 are the latent heats per mol at θ_1 and θ_2 and c is the molal heat capacity of the liquid. The system does work $R(\theta_1-\theta_2)$ if we assume the vapors can be regarded as perfect gases.

Now cool one mol of the vapor at θ_1 and p_1 down to θ_2 at constant pressure p_1 and then expand it at constant temperature θ_2 to pressure p_2 and add it to the vapor in equilibrium with the liquid at θ_2. The heat required for this operation is $C_p(\theta_2-\theta_1)+R\theta_2 \log (p_1/p_2)$. The work done by the system is $R(\theta_2-\theta_1)+R\theta_2 \log (p_1/p_2)$. The final state of the system is the same as at the start so that we have

$$L_1-L_2+\int_{\theta_2}^{\theta_1} c d\theta - R(\theta_1-\theta_2)+C_p(\theta_2-\theta_1)-R(\theta_2-\theta_1)=0.$$

Hence

$$L_1=L_2+C_p(\theta_1-\theta_2)-\int_{\theta_2}^{\theta_1} c d\theta. \tag{1}$$

Also the total change of entropy is zero so that

$$\frac{L_1}{\theta_1}-\frac{L_2}{\theta_2}+\int_{\theta_2}^{\theta_1}\frac{c d\theta}{\theta}-C_p \log\frac{\theta_1}{\theta_2}+R\log\frac{p_1}{p_2}=0. \tag{2}$$

If $\theta_2=0$ equation (1) gives, on putting $C_p=\frac{5}{2}R$ which is true for monatomic gases,

$$L=L_0+\frac{5}{2}R\theta-\int_0^{\theta} c d\theta \tag{3}$$

and from (2) and (3) we get

$$\frac{L_0}{\theta_1}-\frac{5}{2}R\log\theta_1+R\log p_1+\int^{\theta_1}\frac{cd\theta}{\theta}-\frac{1}{\theta_1}\int_0^{\theta_1}cd\theta=$$
$$\frac{L_0}{\theta_2}-\frac{5}{2}R\log\theta_2+R\log p_2+\int^{\theta_2}\frac{cd\theta}{\theta}-\frac{1}{\theta_2}\int_0^{\theta_2}cd\theta$$

so that

$$\log p=-\frac{L_0}{R\theta}+\frac{5}{2}\log\theta+\frac{1}{R\theta}\int_0^{\theta}cd\theta-\int^{\theta}\frac{cd\theta}{R\theta}+i \tag{4}$$

where i is the constant usually called the chemical constant for the liquid.

Now consider a similar reversible cycle for electrons emitted by a metal. Let there be two pieces of the metal maintained at temperatures θ_1 and θ_2 and connected by a fine wire of the same metal. Let them be in equilibrium with electron gas at pressures p_1 and p_2. We suppose these pressures so small that the mutual repulsion of the electrons can be neglected and the electrons regarded as a perfect monatomic gas. Suppose a reversible cycle of operations carried out with the electron gas, precisely similar to that described above. Let the electrical potential inside the metal be zero and let it be ϕ_1 just outside the metal at θ_1 and ϕ_2 just outside that at θ_2. The latent heat of the electrons will be taken to be the heat absorbed at the surface of the metal when one mol of electrons escapes, the potential of the electrons changing from zero in the metal to ϕ outside and the potential of the metal being kept at zero by allowing electrons to flow into it through the wire. We suppose all the operations of the cycle carried out simultaneously so that the number of electrons outside the metal remains constant during the cycle. Then when one mol of electron gas is transferred from the gas at θ_1 to that at θ_2 work $Ne\ (\phi_2-\phi_1)$ has to be done against electrical forces, where e is the charge on one electron and N the number of electrons in one mol. Thus we have

$$L=L_0+Ne(\phi-\phi_0)+\frac{5}{2}R\theta+\int_0^{\theta}Sd\theta \tag{5}$$

or

$$P=P_0+Ne(\phi-\phi_0)+\frac{3}{2}R\theta+\int_0^{\theta}Sd\theta \tag{5a}$$

where S is the heat capacity per Faraday (Ne) of electricity in the metal and P is the internal heat of evaporation. Also as before

$$\log p=-\frac{L_0}{R\theta}-\frac{Ne(\phi-\phi_0)}{R\theta}+\frac{5}{2}\log\theta-\frac{1}{R\theta}\int_0^{\theta}Sd\theta+\int^{\theta}\frac{Sd\theta}{R\theta}+i' \tag{6}$$

where i' is a constant.

Equation (6) differs from the corresponding equation (4) by the term $-Ne\ (\phi-\phi_0)/R\theta$ but the constant i' can nevertheless easily be seen to be equal to the chemical constant for electron gas.

The latent heat of evaporation of the electrons is partly due to the potential difference between a point just outside and one inside the metal. We may suppose $L=w+Ne\phi$ where w is the part of the heat of evaporation due to other than electrical forces. Equation (5) then gives

$$w=w_0+\frac{5}{2}R\theta+\int_0^\theta S d\theta \tag{7}$$

and (6) gives

$$\log p=-\frac{w_0}{R\theta}-\frac{Ne\phi}{R\theta}+\frac{5}{2}\log\theta+\int^\theta\frac{S d\theta}{R\theta}-\frac{1}{R\theta}\int_0^\theta S d\theta+i'. \tag{8}$$

The change of potential ϕ at the surface of the metal may be supposed to take place in a double layer at the surface so that if p' is the pressure just inside this layer we have

$$\log p'=\log p+Ne\phi/R\theta$$

Hence

$$\log p'=-\frac{w_0}{R\theta}+\frac{5}{2}\log\theta+\int^\theta\frac{S d\theta}{R\theta}-\frac{1}{R\theta}\int_0^\theta S d\theta+i'.$$

This equation gives the relation between the temperature and the vapor pressure which the electrons would have if they were uncharged or if ϕ were zero and w_0 is the heat of evaporation they would have at the absolute zero if ϕ were zero.

This equation is therefore precisely similar to equation (4) which gives the vapor pressure of the liquid, so that it is clear that the constants i, and i' are equal respectively to the chemical constants of the liquid and of electron gas. Hence we have

$$\log p=-\frac{(L_0+Ne\,(\phi-\phi_0)+\int_0^\theta S d\theta)}{R\theta}+\frac{5}{2}\log\theta+\int^\theta\frac{S d\theta}{R\theta}+i \tag{9}$$

where i is now the chemical constant for electron gas.

Equations (9) and (5) give

$$L=R\theta^2\frac{d}{d\theta}(\log p)+Ne\theta\frac{d\phi}{d\theta}.$$

Thus it appears that the equation

$$L=R\theta^2\frac{d}{d\theta}(\log p)$$

which gives the latent heat of evaporation of a liquid is not exactly true for the evaporation of electron gas. The previous thermodynamical theories of the emission of electrons given by the writer, O. W. Richardson

and others in which this equation was used are therefore approximately correct only when the term $Ne\theta d\phi/d\theta$ is relatively small.

In Richardson's[6] original theory it was supposed that the internal heat of evaporation was entirely due to electrical forces so that $w_0=0$ and $w=R\theta$. In this case equation (7) gives

$$\frac{3}{2}R\theta=-\int_0^\theta S d\theta$$

so that $S=-\frac{3}{2}R$. This is the value of S that we should expect if the electrons in the metal had the same energy as gas molecules. Putting this value of S in (6) or (9) we get

$$\log p=-Ne\phi/R\theta+\log\theta+\text{constant} \tag{10}$$

which gives Richardson's original equation for I. But as Richardson pointed out, the values found experimentally for S are small compared with R so that as a first approximation we may put $S=0$ and then (7) gives $w=w_0+\frac{5}{2}R\theta$ so that w cannot be less than $\frac{5}{2}R\theta$ and (9) becomes

$$\log p=-\frac{L_0+Ne(\phi-\phi_0)}{R\theta}+\frac{5}{2}\log\theta+i. \tag{11}$$

If we also suppose that ϕ is independent of the temperature so that $\phi-\phi_0=0$ we get

$$\log p=-\frac{L_0}{R\theta}+\frac{5}{2}\log\theta+i \tag{12}$$

which is the equation used by Dushman. L_0 of course is equal to P_0 or to $w_0+Ne\phi_0$. The theory of thermo-electricity indicates that S is probably proportional to the absolute temperature θ. If we assume $S=S_1\theta$ where S_1 is a constant, equation (5) becomes

$$L=L_0+Ne(\phi-\phi_0)+\frac{5}{2}R\theta+\frac{1}{2}S_1\theta^2 \tag{13}$$

and (9) gives

$$\log p=-\frac{L_0+Ne(\phi-\phi_0)}{R\theta}+\frac{5}{2}\log\theta+\frac{S_1\theta}{2R}+i. \tag{14}$$

If I denotes the thermionic emission current we have

$$I=\frac{pe(1-r)}{\sqrt{2\pi mk\theta}} \tag{15}$$

where k is the gas constant for one molecule and r is the reflecting power of the metal for electrons. This equation with (9) or (14) gives I in terms of θ.

[6] Richardson, Camb. Phil. Proc. 11, 286 (1901)

The chemical constant i was calculated on a quantum theory by Sackur[7] and found equal to $i_0+\frac{3}{2}\log M$ where M is the atomic weight of the monatomic gas. Tetrode[8], Stern[9], Planck[10] and Brody[11] have confirmed this result but get a different value for i_0. Lewis[12] favors a value of i_0 which lies between those of Sackur and Stern. All these values are claimed to be supported by the experimental evidence. Since the theory relates to an ideal perfect gas whereas the experimental evidence is got from experiments on real gases which are not perfect we should not expect exact agreement between the theoretical and experimental values. It seems likely that the experimental values should be a little greater than the theoretical values for perfect monatomic gases. If this is admitted then Sackur's theoretical value is most probably the correct one for a perfect gas because it is a little smaller than the experimental values whereas Stern's value is rather larger.

The assumptions made in the calculations of i just mentioned do not inspire much confidence so the following simple method of calculating i, which is based on the established principles of the quantum theory, may be useful. The result obtained agrees with that of Sackur.

Planck in his "Theory of Heat Radiation" Chapter II, calculates the entropy of an ideal monatomic gas by means of his and Boltzmann's probability theory of entropy and shows that

$$i=\log\left\{\frac{Nk^{5/2}(2\pi m)^{3/2}}{\epsilon G}\right\}$$

where G is the size of the region element of the state space for N molecules. It follows as Planck points out that G is proportional to N so that if g is the size of the region element for one molecule then $G=Ng$. This result obtained by Planck before 1911 agrees with Sackur's later result if we put $g=h^3$. Planck however did not then determine the value of g and did not show that it was the same for any monatomic gas.

To determine g imagine a rectangular box with smooth rigid walls containing a single molecule of a monatomic gas. Let the sides of the box be of lengths a, b, and c. Take the origin of coordinates (x, y, z) at one corner of the box and let the sides a, b, c lie along the axes x, y, z respectively. The molecule will move in the box along straight lines and when

[7] Sackur, Ann. der Physik **40**, 67 (1913)
[8] Tetrode, Ann. der Physik **38**, 434; **39**, 255 (1912)
[9] Stern, Zeit. f. Electrochemie **25**, 66 (1919)
[10] Planck, Berlin Akad. 1916 p. 653
[11] Brody, Zeit. f. Physik **6**, 79 (1921); cf. Bull. Nat. Research Council, "Quantum Theory," Adams
[12] Lewis, Phys. Rev. **3**, 92 (1914)

it strikes a side of the box its velocity component perpendicular to that side will be reversed. The state space for this molecule will be of six dimensions $m\dot{x}$, $m\dot{y}$, $m\dot{z}$, x, y, and z. The path of the molecule in the $(m\dot{x}, x)$ plane goes around a rectangle $ABCD$, with AB and CD parallel to the axis of x. At A the molecule is at the end of the box where $x=0$ and then moves along AB since $\dot{x}$ is constant. When $x=a$ it collides with the other end of the box at B and its velocity $\dot{x}$ is reversed at P so the path goes to C. The path then goes along CD and back to A when the collision at $x=0$ takes place. The motion is thus a cyclic one and the frequency is $\dot{x}/2a$. According to the W. Wilson-Sommerfeld quantum condition which is supposed to apply to any cyclic motion of a single electron or atom we have

$$\int pdq = \int m\dot{x}dx = n_1 h$$

where n_1 is an integer. The area $ABCD$ must therefore be $n_1 h$ so that

$$2m\dot{x}a = n_1 h$$

or

$$\dot{x} = n_1 h/2ma.$$

In the same way we get $\dot{y}=n_2 h/2mb$ and $\dot{z}=n_3 h/2mc$. The kinetic energy of the molecule is therefore

$$\tfrac{1}{2}m(\dot{x}^2+\dot{y}^2+\dot{z}^2) = \frac{h^2}{8m}\left(\frac{n_1^2}{a^2}+\frac{n_2^2}{b^2}+\frac{n_3^2}{c^2}\right).$$

This result was obtained by Brody[11] by a similar method. The region element on the plane $(m\dot{x}, x)$ is therefore of area h and it is made up of two rectangular strips of length a and total breadth h/a. The six dimensional region element is therefore a block with sides a, b, c, h/a, h/b and h/c so that its volume is h^3. Hence $G=Nh^3$ and

$$i = \log\left\{\frac{k^{5/2}(2\pi m)^{3/2}}{\epsilon h^3}\right\}.$$

This result becomes the same as Stern's which was adopted by Dushman, if the ϵ is omitted, so it is less than Stern's value by unity.

Brody's calculation which gives Stern's value of i_0 really shows that Stern's value is too large. He takes the number of ways in which a gas can have energy exactly E equal to the number in which its energy can be between E and $E+1$ which clearly enormously overestimates the number of ways and so must give too large a value of the entropy and hence also of i_0.

Using the value just found for i we obtain from equations (9) and (15) the exact equation for the thermionic emission current I,

$$I = \frac{2\pi mek^2(1-r)}{\epsilon h^3}\theta^2\epsilon^{-\left\{\frac{L_0+Ne(\phi-\phi_0)+\int_0^\theta S d\theta}{R\theta}-\int^\theta \frac{Sd\theta}{R\theta}\right\}}. \tag{16}$$

If we suppose the metal does not reflect any electrons so that $r=0$ and that $\phi-\phi_0=0$ and also that $S=0$ we get

$$I=\frac{2\pi me k^2}{\epsilon h^3}\theta^2\epsilon^{-L_0/R\theta} \tag{17}$$

If Stern's value of i is preferred the ϵ in the denominator may be omitted from (16) and (17).

The reflecting power r is probably not large for slow electrons and ϕ probably does not vary much with the temperature so that this investigation may be said to confirm (17) as a first approximation for I.

The very accurate measurements of I which have recently been made by Davisson and Germer,[13] Schlichter[14] and others seem to justify the working out of an accurate expression for it.

Dushman shows that the results obtained for tungsten and platinum when put in the equation

$$I=\frac{2\pi me k^2}{h^3}\theta^2\epsilon^{-b_0/\theta} \tag{18}$$

give very constant values of b_0 over considerable ranges of temperature. If we suppose that

$$Ne(\phi-\phi_0)+\int_0^\theta S d\theta-\theta\int^\theta\frac{S d\theta}{\theta}+R\theta\left\{1-\log(1-r)\right\}=0. \tag{19}$$

Then since $b_0=L_0/R$ (16) becomes identical with (18) so that if (19) is true then Dushman's equation is exact. Davisson's results for tungsten with equation (18) give values b_0 which do not vary from the average value 51860 by more than 60 for temperatures from 1935 to 2306. The value of the specific heat of electricity for most metals is about -1000 ergs per e.m.u. at ordinary temperatures. This gives for S about -0.2 calories per Faraday. If we suppose $S=S_1\theta$ then S_1 must be about -0.001. This gives $\int_0^{2000} S d\theta=-2000$ calories and $\int_{1900}^{2300} S d\theta=-800$. $\theta\int_0^\theta\frac{S d\theta}{\theta}$ is about double $\int_0^\theta S d\theta$ so that the terms containing S in equation (19) are about equal to 2000 calories and the values of these terms increases by about 800 in the range from 1900 to 2300. This is about seven times the variation in $L_0=2b_0$ got from Davisson's results so that to explain them it is necessary to suppose that the changes in ϕ and perhaps r with the temperature compensate for the changes in the integrals of S. Of course if S is not propertional to θ these variations would be smaller but it is clear that Davisson's results are sufficiently accurate to make it worth while to use

[13] Germer, Phys. Rev. **20**, 300 (1922)
[14] Schlichter, Ann. der Phys. **47**, 573 (1915)

the exact expression for I in place of the first approximation. It seems probable that ϕ changes with the temperature in such a way as to more or less completely compensate for the changes in the integrals of S and the term $R\theta(1-\log(1-r))$. To test the exact equation (16) it will be necessary to have accurate measurements of I over a large range of temperature and approximate values of S, r and $\phi-\phi_0$ for the same range.

$\phi-\phi_0$ is equal to the contact difference of potential between the hot metal and the same metal at the absolute zero. Unless some idea of the value of this quantity can be obtained independently it will always be possible to make any experimental results for I fit the equation (16) by supposing $\phi-\phi_0$ to vary with the temperature in the necessary way. If it is found that equation (18) exactly represents the experimental results then it will be necessary to conclude that the relation (19) between ϕ, S, r and θ is true and it may be possible to work out a theoretical basis for this equation.

RICE INSTITUTE,
HOUSTON, TEXAS.
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CURRENTS LIMITED BY SPACE CHARGE BETWEEN CONCENTRIC SPHERES

By Irving Langmuir and Katharine B. Blodgett

Abstract

Limiting current between concentric spheres; calculation of the function $a=f(r/r_0)$ in the space charge equation $i=(4\sqrt{2}/9)\sqrt{(e/m)}V^{3/2}/a^2$.—The coefficients of the first six terms of a series for a were determined, and a^2 calculated from this series. The results were checked by an integration method which was also used to calculate values in the region where the series failed. For an emitter of radius r_0 inside a collector of radius r, values of a^2 when $\log (r/r_0)>6.4$ are given by the equation

$$\tfrac{1}{2}a^2=0.112 \log (\log r/r_0)+\tfrac{1}{3} \log (r/r_0)+0.152.$$

Where the collector is the inside sphere, values of a^2 for $r_0/r>9$ are given by the equation $(\frac{1}{2}a^2)^{2/3}=1.11\ (r_0/r)-1.64$. It is shown that when the collector is the inside sphere the potential distribution near the collector is unaltered if the emitter is replaced by a non-emitting sphere with a diameter .677 times the original diameter.

Limiting current between coaxial cylinders and between concentric spheres.—Equations are derived for the current in terms of the radius of curvature of the emitter. It is shown that at a surface in space four-fifths of the distance from the emitter to the collector the current density is independent of the radius of curvature when r/r_0 or $r_0/r<2$; and in the case of coaxial cylinders with the emitter inside this holds true even when $r/r_0=20$.

THE problem of the calculation of thermionic currents limited by space charge has to deal with three simple cases, those of parallel planes, coaxial cylinders, and concentric spheres. These three cases have the characteristic that when an electron current is flowing, the lines of force and the paths of the electrons coincide. Parallel planes[1] and coaxial cylinders[2] have been considered in previous papers, and the equations have been given for calculating the currents for these surfaces. Although it is easy to construct apparatus in which the conditions approximate closely those of the cylindrical case, it is difficult to build devices in which the heated cathode takes the form of a sphere.

Recently space charge equations have been used in a new line of experimental work[3] to measure the intensity of ionization in gaseous discharges in which a positive ion sheath forms around the negatively charged electrode and the current is limited by space charge. Surfaces of different shapes have been used for electrodes, and since the sphere has proved

[1] Langmuir, Phys. Rev. **2**, 450 (1913); Phys. Zeits. **15**, 348, (1914)

[2] Langmuir and Blodgett, Phys. Rev. **22**, 347 (1923)

[3] Langmuir, Science, **58**, 290 (1923); Gen. Elec. Rev. **26**, 731 (1923); Journ. Franklin Inst. **196**, 751 (1923)

to be particularly suitable, the space charge equations for spherical electrodes have assumed practical importance. The development of these equations and the calculation of the numerical values of the function α which they involve will be given in this paper. The derivation has been made with the intention of using the equations to calculate the flow of either electrons or positive ions, and for this reason the general case has been developed in which the current flows from an *emitter* to a *collector* without regard to the direction of the voltage between the electrodes. Thus for calculations on ionization in gaseous discharges the outer edge of the positive ion sheath itself is the emitter of ions and the negative electrode within the sheath is the collector.

For the case of space charge between concentric spheres Poisson's equation becomes

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dV}{dr}\right)=4\pi\rho \tag{1}$$

where V is the potential at a point distant r from the center, and ρ is the electron space charge. If i is the total thermionic current, v the velocity of electrons or ions at the distance r, and e and m the charge and mass of an electron or ion,

$$i=4\pi r^2\rho V. \tag{2}$$

If we neglect the initial velocities of the particles we have

$$\tfrac{1}{2}mv^2=Ve \tag{3}$$

where V is measured from the surface of the emitter. Combining Eqs. (1), (2), and (3) gives

$$\frac{d}{dr}\left(r^2\frac{dV}{dr}\right)=i\sqrt{\frac{m}{2eV}}. \tag{4}$$

This equation, like the similar equation for coaxial cylinders, probably cannot be directly integrated, but a result can be obtained in terms of a series. The final solution takes the form

$$i=\frac{4\sqrt{2}}{9}\sqrt{\frac{e}{m}}\,\frac{V^{3/2}}{\alpha^2} \tag{5}$$

where α is a function of the ratio of the radii r and r_0 of the spheres, r_0 being the radius of the emitter. It is seen from this equation that the current is independent of the actual sizes of the spheres since the radii appear only in a ratio.

Calculation of α

An equation in α can be obtained by substituting Eq. (5) in Eq. (4) and placing

$$\gamma=\log(r/r_0) \tag{6}$$

This gives

$$3\alpha\frac{d^2\alpha}{d\gamma^2}+\left(\frac{d\alpha}{d\gamma}\right)^2+3\alpha\frac{d\alpha}{d\gamma}-1=0 \tag{7}$$

From this equation the values of α can be obtained in terms of a series. The coefficients of the first six terms of the series were obtained by a method described in a recent paper,[2] which makes use of Maclaurin's series in the neighborhood of $\gamma=0$. The series for α thus calculated is

$$\alpha=\gamma-0.3\gamma^2+0.075\gamma^3-0.0143182\gamma^4+0.0021609\gamma^5-0.00026791\gamma^6+\cdots \tag{8}$$

The first three coefficients are exact and the last three are each rounded off in the last figure.

Case where $r/r_0>1$ (Emitter inside of collector). For values of r/r_0 up to 5, α could be calculated accurately to three places of decimals from the series in Eq. (8). For the larger values, however, the six terms were entirely insufficient, and an integration process was used to complete the calculations. This process was applied to the equation obtained from Eq. (7) by making the substitution

$$y=\tfrac{1}{2}\alpha^2 \tag{9}$$

which gives

$$3\frac{d^2y}{d\gamma^2}-\frac{1}{y}\left(\frac{dy}{d\gamma}\right)^2+3\frac{dy}{d\gamma}-1=0. \tag{10}$$

The method employed was described in the recent paper referred to above, and consists essentially in substituting approximate values of y and $dy/d\gamma$ in Eq. (10), solving the equation for $d^2y/d\gamma^2$, and integrating the values thus obtained for new values of y and $dy/d\gamma$ which will be more nearly correct than the approximate values substituted at the beginning of the process. These calculations were made with y in the region $\gamma=1.0$ to $\gamma=2.2$, and the values of y obtained as the result of integration agreed exactly with those obtained from the series. The process was then used to calculate y in the range $\gamma=2.2$ to $\gamma=26.8$ where the series was insufficient. The results of these calculations are given in Table I.

The following empirical equation was found to fit the calculated values of y, $dy/d\gamma$ and $d^2y/d\gamma^2$ with a high degree of accuracy for values of γ greater than 11.8,

$$y=0.112\log\gamma+\tfrac{1}{3}\gamma+0.152. \tag{11}$$

The values of y given by this equation have an error of .48 per cent at $\gamma=6.4$ and .025 per cent at $\gamma=11.8$.

Table II gives the complete range of values of α^2 up to $r/r_0=100{,}000$. The values corresponding to $r/r_0>5$ were obtained from interpolations for α from Table I, using Newton's interpolation formula.

Case where $r/r_0<1$ (Emitter outside of collector). The series in Eq. (8) that was used to calculate α in the preceding case is also applicable in the inverted case where the cathode is the outside cylinder, but since γ is now negative the signs of the alternate terms are changed. In this case, also, the integration process was used to calculate α for the larger values of γ.

TABLE I

γ	$dy/d\gamma$	$y=\frac{1}{2}\alpha^2$	α
2.2	.4512	.8424	1.2980
2.4	.4435	.9319	1.3652
2.6	.4354	1.0198	1.4281
2.8	.4275	1.1061	1.4873
3.0	.4198	1.1908	1.5432
3.2	.4126	1.2741	1.5963
3.4	.4060	1.3559	1.6468
3.7	.3970	1.4763	1.7183
4.0	.3891	1.5942	1.7856
4.3	.3825	1.7099	1.8493
4.6	.3767	1.8238	1.9099
4.9	.3720	1.9361	1.9678
5.2	.3678	2.0471	2.0234
5.8	.3615	2.2658	2.1288
6.4	.3569	2.4812	2.2276
7.0	.3536	2.6944	2.3214
7.6	.3510	2.9057	2.4107
8.2	.3493	3.1157	2.4963
8.8	.3476	3.3249	2.5787
11.8	.3433	4.3607	2.9532
14.8	.3410	5.3867	3.2823
17.8	.3397	6.4077	3.5799
20.8	.3387	7.4252	3.8536
23.8	.3380	8.4402	4.1086
26.8	.3375	9.4534	4.3482

The equation which was used in this process was obtained by combining Eqs. (6) and (10) and placing $r_0/r=\sigma$, which gives

$$3\frac{d^2y}{d\sigma^2}-\frac{1}{y}\left(\frac{dy}{d\sigma}\right)^2-\frac{1}{\sigma^2}=0 \qquad (12)$$

The results of calculations using the integration process in the range $\sigma=7$ to $\sigma=22$ are given in Table III.

In the neighborhood of $\sigma=22$, the term $1/\sigma^2$ in Eq. (12) is decreasing rapidly and has already become only 0.7 per cent of the second term, so that a solution of the equation neglecting the term $1/\sigma^2$ gives a good

approximation formula for y which may be used to obtain values of α in the region beyond $\sigma=22$. The complete solution of

$$3\frac{d^2y}{d\sigma^2}-\frac{1}{y}\left(\frac{dy}{d\sigma}\right)^2=0 \tag{13}$$

is

$$y^{2/3}=A\sigma+B \tag{14}$$

TABLE II

α^2 as function of radius.

r_0 = radius of emitter; r = radius at any point P;
α^2 applies to case where P is outside emitter, $r>r_0$;
$(-\alpha)^2$ applies to case where P is inside emitter, $r_0>r$.

$\frac{r}{r_0}$ or $\frac{r_0}{r}$	α^2	$(-\alpha)^2$	$\frac{r}{r_0}$ or $\frac{r_0}{r}$	α^2	$(-\alpha)^2$
1.0	0.0000	0.0000	6.5	1.385	13.35
1.05	.0023	.0024	7.0	1.453	15.35
1.1	.0086	.0096	7.5	1.516	17.44
1.15	.0180	.0213	8.0	1.575	19.62
1.2	.0299	.0372	8.5	1.630	21.89
1.25	.0437	.0571	9.0	1.682	24.25
1.3	.0591	.0809	9.5	1.731	26.68
1.35	.0756	.1084	10	1.777	29.19
1.4	.0931	.1396	12	1.938	39.98
1.45	.1114	.1740	14	2.073	51.86
1.5	.1302	.2118	16	2.189	64.74
1.6	.1688	.2968	18	2.289	78.56
1.7	.208	.394	20	2.378	93.24
1.8	.248	.502	30	2.713	178.2
1.9	.287	.621	40	2.944	279.6
2.0	.326	.750	50	3.120	395.3
2.1	.364	.888	60	3.261	523.6
2.2	.402	1.036	70	3.380	663.3
2.3	.438	1.193	80	3.482	813.7
2.4	.474	1.358	90	3.572	974.1
2.5	.509	1.531	100	3.652	1144
2.6	.543	1.712	120	3.788	1509
2.7	.576	1.901	140	3.903	1907
2.8	.608	2.098	160	4.002	2333
2.9	.639	2.302	180	4.089	2790
3.0	.669	2.512	200	4.166	3270
3.2	.727	2.954	250	4.329	4582
3.4	.783	3.421	300	4.462	6031
3.6	.836	3.913	350	4.573	7610
3.8	.886	4.429	400	4.669	9303
4.0	.934	4.968	500	4.829	13015
4.2	.979	5.528	600	4.960	
4.4	1.022	6.109	800	5.165	
4.6	1.063	6.712	1000	5.324	
4.8	1.103	7.334	1500	5.610	
5.0	1.141	7.976	2000	5.812	
5.2	1.178	8.636	5000	6.453	
5.4	1.213	9.315	10000	6.933	
5.6	1.247	10.01	30000	7.693	
5.8	1.280	10.73	100000	8.523	
6.0	1.311	11.46			

The values of A and B were derived from the data in Table III, with the result

$$y^{2/3}=1.11\sigma-1.64. \tag{15}$$

Values of y obtained from this equation have an error of 0.5 per cent at $\sigma=9$ and 0.025 per cent at $\sigma=18$. Table II gives the complete range of values of α^2 for this case up to $r_0/r=500$. Eq. (15) was used for the calculations in the range $r_0/r=22$ to 500.

TABLE III

$\sigma=r_0/r$	$dy/d\sigma$	$y=\frac{1}{4}\alpha^2$	α
7.0	2.0454	7.675	3.918
7.5	2.1376	8.721	4.176
8.0	2.2261	9.812	4.430
8.5	2.3113	10.947	4.679
9.0	2.3935	12.123	4.924
9.5	2.4730	13.340	5.165
10.0	2.5501	14.596	5.403
12.	2.8379	19.988	6.323
14.	3.0990	25.930	7.201
16.	3.3400	32.371	8.046
18.	3.5646	39.280	8.863
20.	3.7760	46.622	9.656
22.	3.9761	54.378	10.429

Low values of α^2 for either the direct or inverted case where r/r_0 or $r_0/r<1.4$, may be conveniently calculated from Eq. (16) which is derived in the following manner. Put $\epsilon=(r_0/r)-1$ and expand $\gamma=-\log(r_0/r)$ into a series in terms of ϵ. Substitute this value of γ in the equation obtained by squaring Eq. (8) and as a result

$$\alpha^2=\epsilon^2-\frac{2}{5}\epsilon^3+\frac{77}{300}\epsilon^4-\frac{313}{1100}\epsilon^5+\cdots \tag{16}$$

Logarithmic differentiation of Eq. (5), considering i as constant, gives

$$2\frac{d\alpha}{\alpha}=\frac{3}{2}\frac{dV}{V}. \tag{17}$$

Logarithmic differentiation of Eq. (15) combined with Eq. (9) gives

$$\frac{4}{3}\frac{d\alpha}{\alpha}=\frac{1.11\,d\sigma}{1.11\sigma-1.64}. \tag{18}$$

Combining this with Eq. (17) and substituting $\sigma=r_0/r$,

$$\frac{dV}{V}=-\frac{dr}{r^2}\Big/\left(\frac{1}{r}-\frac{1.477}{r_0}\right). \tag{19}$$

In the case of two concentric spheres, neither of which is emitting current, the voltage at any point of radius r is

$$V=A\left(\frac{1}{r}-\frac{1}{r_1}\right) \tag{20}$$

where V is measured with respect to the sphere of radius r_1. Logarithmic differentiation of Eq. (20) gives

$$\frac{dV}{V}=-\frac{dr}{r^2}\Big/\left(\frac{1}{r}-\frac{1}{r_1}\right). \tag{21}$$

Comparing Eqs. (19) and (21) we see that they become identical for all values of r if we place

$$r_1=0.677\ r_0. \tag{22}$$

Thus when current emitted by a spherical electrode is being collected by an inner concentric sphere of small diameter, the effect of space charge is to make the potential distribution near the collector the same as it would be if the outer sphere were not emitting current and were given a diameter 67.7 per cent of the original diameter. A similar ratio of diameters for the case of cylinders was given in the previous paper and is 0.707.

Comparison of Equations for Planes, Cylinders and Spheres

The equations given in this paper and two preceding papers for calculating thermionic currents limited by space charge are as follows:

Parallel planes (i_a = current per unit area)

$$i_a=\frac{\sqrt{2}}{9\pi}\sqrt{\frac{e}{m}}\ \frac{V^{3/2}}{x^2} \tag{23}$$

Coaxial cylinders (i_l = current per unit length)

$$i_l=\frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\ \frac{V^{3/2}}{r\beta^2} \tag{24}$$

Concentric spheres (i = total current)

$$i=\frac{4\sqrt{2}}{9}\sqrt{\frac{e}{m}}\ \frac{V^{3/2}}{a^2} \tag{25}$$

If these three equations are written in the same form by substituting $i_l/(2\pi r_0)=i_a$ and $i/(4\pi r_0^2)=i_a$, they become

for parallel planes,

$$i_a=D/x^2; \tag{26}$$

for coaxial cylinders,

$$i_a=D/(r_0r\beta^2); \tag{27}$$

for concentric spheres,

$$i_a=D/(r_0^2a^2); \tag{28}$$

where

$$D=\frac{\sqrt{2}}{9\pi}\sqrt{\frac{e}{m}}V^{3/2}. \tag{29}$$

If i is expressed in amperes per cm^2, V in volts, x and r in cm, and e and m are the charge and mass respectively of an electron, D has the value

$$D=2.336\times10^{-6}V^{3/2}$$

If e and m are the charge and mass of an ion,

$$D=5.455\times10^{-8}V^{3/2}/\sqrt{M}$$

where M is the molecular weight of the ions (oxygen atom = 16).

Consider the case of two concentric spheres that are very close together so that their surfaces are almost parallel. If we put $r=(r_0+x)$ and $b=x/r_0=(r/r_0-1)$ we can write a series for α^2 similar to the series in Eq. (16) as follows

$$\alpha^2=b^2-\frac{8}{5}b^3+\frac{617}{300}b^4-\ldots \tag{30}$$

This value of α^2 may be substituted in Eq. (28) and it is then seen that when b becomes so small that all the terms in the series except the first are negligible, the equation becomes identical with Eq. (26) for parallel planes.

In the same way a series for β^2 can be derived, which is

$$\beta^2=b^2-\frac{9}{5}b^3+\frac{123}{50}b^4-\ldots \tag{31}$$

and this can be substituted in Eq. (27) which will also become identical with the equation for parallel planes when b is very small.

Where the surfaces of cylinders and spheres are farther apart so that the second and third terms of the series in Eqs. (30) and (31) become important and the conditions no longer closely approximate those of parallel planes, these series enable us to obtain equations for the current in terms of the total curvature of the *emitting* surfaces. This total curvature ρ_0 in the case of the emitting cylinder is $\rho_0=1/r_0$, and for the sphere is $\rho_0=2/r_0$. Combining $r=(r_0+x)$ with Eq. (31) and substituting the value of ρ_0 for a cylinder, we have

$$r_0r\beta^2=x^2\left(1-\frac{4}{5}x\rho_0+\frac{33}{50}x^2\rho_0^2-\ldots\right) \tag{32}$$

Similarly from Eq. (30) we have for spheres

$$r_0^2\alpha^2=x^2\left(1-\frac{4}{5}x\rho_0+\frac{617}{1200}x^2\rho_0^2-\ldots\right) \tag{33}$$

We now see that the equations for cylinders and spheres in terms of the total curvature of the emitting surface have the first two terms identical. By expanding the reciprocal of the series in Eq. (32) we obtain an expression for $1/(r_0r\beta^2)$, in which the second term is $+4/5$ $(x\rho_0)$ but the

third term is only $-0.02\,x^2\rho^2$ which is 3 per cent of the third term in Eq. (32). Carrying through a similar process for Eq. (33) the third term becomes $0.126\,x^2\rho^2$. Substituting these values for $1/(r_0r\beta^2)$ and $1/(r_0^2a^2)$ in Eqs. (27) and (28) and neglecting the third terms of the expansions, we have

$$i_a=\frac{\sqrt{2}}{9\pi}\sqrt{\frac{e}{m}}\frac{V^{3/2}}{x^2}\left(1+\frac{4}{5}x\rho_0\right) \tag{34}$$

which is the equation for parallel planes with a first order correction term for curved surfaces in terms of the curvature of the surface.

But it was arbitrary when defining the current per unit area and the total curvature to choose the area and curvature of the surface of the *emitter*. We may just as well choose the surface of the collector or any surface between them. We shall consider the general case where the current is measured per unit area of a surface of radius $r_1=(r_0+kx)$ for which the total curvature is $\rho_1=\rho_0/(1+\rho_0kx)$ for a cylinder or $\rho_1=\rho_0/(1+\frac{1}{2}\rho_0kx)$ for a sphere.

In this case from Eqs. (27) and (28) the current per unit area of the new surface is $i_a=D/[(r_0+kx)r\beta^2]$ for cylinders and $i_a=D/[(r_0+kx)^2a^2]$ for spheres. Eqs. (32) and (33) will then become

$$(r_0+kx)r\beta^2=x^2\left[1+\left(k-\frac{4}{5}\right)x\rho_1+\left(k^2-\frac{8}{5}\,k+\frac{33}{50}\right)x^2\rho_1^2+---\right] \tag{35}$$

and

$$(r_0+kx)^2a^2=x^2\left[1+\left(k-\frac{4}{5}\right)x\rho_1+\left(\frac{3}{4}k^2-\frac{6}{5}k+\frac{617}{1200}\right)x^2\rho_1^2+---\right]. \tag{36}$$

It now becomes apparent that for $k=4/5$ the second term in both series will vanish for all values of $x\rho_1$, and the coefficients of $x^2\rho_1^2$ will be small, having the value .02 for cylinders and .0342 for spheres. This means that for all values of $x\rho_1$ that make the third terms negligible, the current *per unit area of a surface four-fifths of the distance from the emitter to the collector* is the same as for parallel plane electrodes spaced the same distance apart as the two curved electrodes.

We have thus determined a surface in space at which the current per unit area is the same whether the electrodes are plane or curved, provided that $.03x^2\rho_1^2$ is small compared to unity. This suggests that it may be possible to locate such a surface in every instance by properly choosing the value of k. At this surface, the equations for parallel planes, coaxial cylinders, and concentric spheres must become identical, and therefore, substituting (r_0+kx) for r_0, we have from Eqs. (26) and (27)

$$x^2=(r_0+kx)r\beta^2 \tag{37}$$

from which

$$k=\frac{x}{r\beta^2}-\frac{r_0}{x}. \tag{38}$$

Similarly in the case of spheres

$$x^2=(r_0+kx)^2a^2 \tag{39}$$

from which

$$k=\frac{1}{a}-\frac{r_0}{x} \tag{40}$$

Since $x=(r-r_0)$, Eqs. (38) and (40) may be written with the radii of the curved surfaces appearing in each case only as a ratio. Values of k calculated from these equations are given in Table IV.

TABLE IV

Values of k as a function of the radii

$\frac{r}{r_0}$ or $\frac{r_0}{r}$	Cylinder $r/r_0>1$	Cylinder $r/r_0<1$	Sphere $r/r_0>1$	Sphere $r/r_0<1$
1.0	0.8000	0.8000	0.8000	0.8000
1.2	.7970	.8039	.7877	.8122
1.5	.7932	.8093	.7718	.8268
2.0	.7904	.8171	.7513	.8450
5.0	.7935	.8455	.6862	.8959
10	.8090	.8677	.6393	.9260
20	.8340	.8883	.5959	.9490
100	.9081	.9258	.5132	.9805
∞	1.0000	1.0000	.0000	1.0000

Consider the case of two coaxial cylinders where the emitter is the inner one and has a radius 1 while the collector has a radius 20. From Table IV $k=.834$, and a surface 83.4 per cent of the distance from the emitter has a radius $r_1=16.846$. The current per unit area of this surface by Eq. (27) is $i_a=D/(16.846r\beta^2)$. Substituting the value $\beta^2=1.0715$ when $r/r_0=20$ we have $i_a=D/361$ for the correct value of the current, which is the same value as $i_a=D/(19)^2$ for the current between two parallel planes.

If we had given k the approximate value 0.8 we should have had $i_a=D/347.2$ for the current per unit area of a surface with radius $r_1=16.2$. This differs from the value of current between parallel planes by 4 per cent, and since this error is $(.8x-.834x)/(r_0+.834x)$ it is clear that it is less than the error in k. Thus in this case for a range of ratio of radii from 1/1 to 1/20 the current per unit area of a surface four-fifths of the distance from the emitter is the same as the current between parallel planes within an error of 4 per cent, and over half the range the error is less than 1 per cent.

On the other hand in the case of coaxial cylinders with the emitter outside, Table IV shows that k departs much more rapidly from the value 0.8. The error introduced into calculations of current by choosing $k=0.8$ instead of the exact value k_a from the Table is $(.8x-k_ax)/(r_0+k_ax)$ where $x=(r-r_0)$ is now negative. This error in current is proportional to the error in k as k_a is to $(r_0/x+k_a)$, which shows that calculations of current using $k=0.8$ may be made with an error less than that of k only up to $r_0/r=2.55$, and above that point the error is greater than that of k, becoming infinitely great as r_0/r approaches infinity.

In the case of spheres the value $k=0.8$ yields an error of 5.6 per cent for $r/r_0=2.0$ where the emitter is inside, and 7.9 per cent for $r_0/r=2.0$ where the emitter is outside. Thus when current is flowing in either direction between any curved surfaces where the radius of the outer surface is not more than twice the radius of the inner, the amount of current flowing per unit area of a surface four-fifths of the distance from the emitter to the collector is very nearly the same as the current between parallel planes. In the case of coaxial cylinders with the emitter inside this same rule applies with similar accuracy even when the radius of one is twenty times the radius of the other.

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THE MAGNETOSTRICTION OF A MAGNETITE CRYSTAL

By C. W. Heaps

Abstract

Magnetostriction of an octagonal magnetite crystal along three axes was measured in fields up to 5000 gauss. The curves obtained are all similar in form, first convex towards the *H* axis, then concave, tending toward a maximum near 5000 gauss. With a longitudinal field of 5000 gauss, the digonal axis expands $30(10)^{-4}$ per cent, the trigonal axis $12(10)^{-4}$ per cent, and the tetragonal axis contracts about $4(10)^{-4}$ per cent. With an equal transverse field the percentage changes are a contraction of $44(10)^{-4}$, a contraction of $28(10)^{-4}$ and an expansion of $4(10)^{-4}$, respectively. Tests indicated that the effect perpendicular to a plane is independent of the direction of the field in that plane. No departure from cubic symmetry was established. To explain these results a *model of the magnetic element* in magnetite is suggested, similar to Ewing's recent model. The experiments favor the view that the rotating magnetic element is a group of non-parallel electron orbits inside the atom.

Permeability of a magnetite crystal was roughly determined to vary from 1.2 to 1.38 as the field strength increased to 5000 gauss.

IN a recent paper[1] the writer described some magnetostrictive effects obtained with a crystal of magnetite ground into the form of a sphere. The experiments, however, were not of a definite enough nature to permit the exact correlation of the magnetostriction with the directions of the crystallographic axes. The great differences in the character of the phenomena for different directions in the sphere made the location of these axes with respect to the magnetostriction a matter of some importance. Further experiments have now been performed and the magnetostriction definitely correlated with the axes.

The apparatus for measuring dimension changes, except for a few modifications made in order to facilitate the adjusting of the specimen, was the same as described in the previous paper. An electromagnet smaller than the one of the previous experiments was used in this later work. It had pole-pieces 5.8 cm in diameter and these were kept 3.3 cm apart throughout the work. The field, therefore, was probably not as uniform as in the case of the larger magnet. Tests with a flux-meter and search coil showed the field midway between the pole-pieces to be somewhat less than 2 per cent smaller than the field very near the pole-pieces.

The magnetite crystal was an octahedron from Henry County, Virginia. It was quite perfect, with principal axes about 1.8 cm long. Before

[1] Heaps, Phys. Rev. **22**, 486, 1923

making measurements on this crystal the corners and edges were rounded off by grinding. It was thus easier to clamp the crystal in the measuring device; also the specimen was made more nearly spherical and the intensity of magnetization presumably more uniform.

Magnetostriction of the specimen was investigated with respect to three different crystallographic axes, the tetragonal, the trigonal, and the digonal. Magnetite belongs to the cubic system, the eight faces of the octahedron being equilateral triangles. The three fundamental axes of the cube, the tetragonal axes, join opposite vertices of the octahedron. The four trigonal axes, each of which connects opposite vertices of the elementary cube, have the direction of the normals to the faces of the octahedron. The six digonal axes are each perpendicular to a pair of parallel edges of the octahedron.

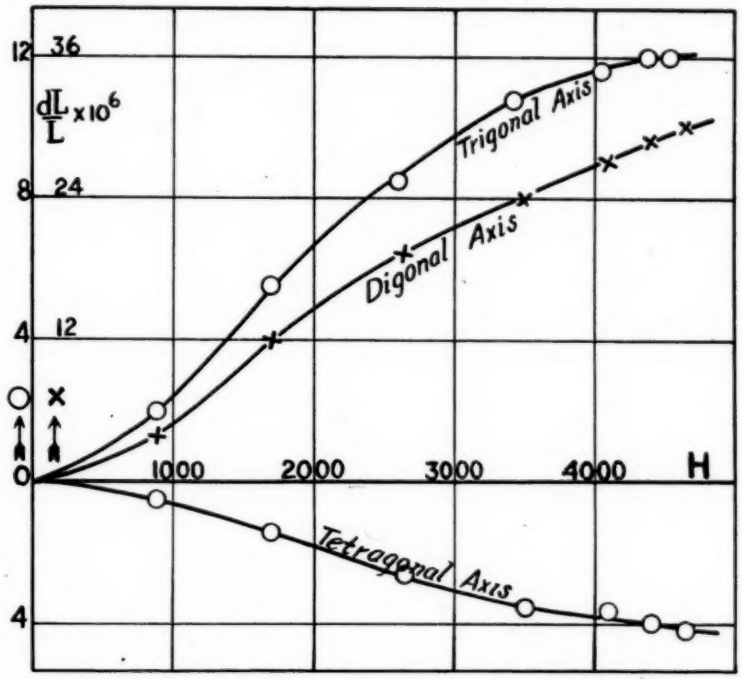

Fig. 1. Longitudinal magnetostriction along different axes.

The curves of Fig. 1 represent the magnetostriction obtained in the direction of the field for different values of the magnetic field H (measured in the absence of the crystal). Here dL/L is the change of length of an axis divided by the total length of that axis. The longitudinal magnetostriction along the digonal, trigonal, and tetragonal axes varies in much the same way with the field as the latter is increased, but the contraction

(plotted below the H axis) along the tetragonal axis is smaller than the expansions (plotted above the H axis) which occur for the same fields along the trigonal and digonal axes. It is to be noted that two scales are used, the curve for expansion of the digonal axis being plotted with reference to the scale giving the larger values.

Fig. 2 gives the magnetostriction along three different axes, the field being for each curve normal to the axis specified on the curve. Contractions are plotted below the H axis, expansions above the axis. It appears

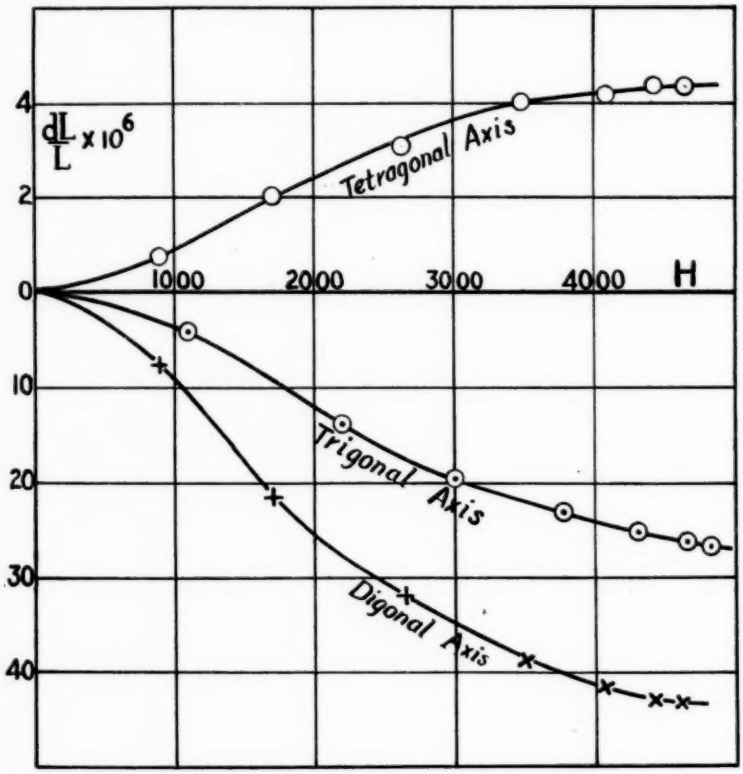

Fig. 2. Transverse magnetostriction along different axes.

that for transverse magnetic fields the tetragonal axis expands while the trigonal and digonal axes suffer contractions of considerably larger magnitudes.

The curves of Figs. 1 and 2 are all similar in appearance. They are also similar to the curves for a magnetite sphere which are given in the previous paper. The curves for the sphere, however, are plotted against magnetic induction and are extended to higher values of the field so that the existence of maxima is more clearly indicated than in Figs. 1 and 2.

The field instead of the induction is plotted in the present work because of the difficulty of measuring the latter quantity accurately when the specimen is not spherical. Approximately correct values were obtained, however, by using a fluxmeter connected to five turns of wire wound around the specimen. In this way the permeability of the magnetite was found to vary from 1.2 to 1.38 for the field values plotted in the curves.

In its magnetic properties magnetite has been found[2] to show departures from cubic symmetry. To investigate this question the transverse magnetostriction for the different tetragonal and trigonal axes was measured. It was found that slight departures from accuracy in the setting of the crystal caused considerable changes in the magnitude of the magnetostriction so that small deviations from cubic symmetry could not be detected easily. It seemed possible, however, that one of the tetragonal axes expanded more than the others under the influence of the field.

From the curves of Figs. 1 and 2, and on the assumption of cubic symmetry, the curves of Fig. 3 were constructed. Here the maximum magnetic field is supposed to be rotated in one of the planes of symmetry of the crystal, the angle θ between the tetragonal axis and the field being plotted as abscissas, the corresponding magnetostriction as ordinates. From these curves it appears that a longitudinal field rotated in the axial plane (100) produces two maxima of extension and two maxima of contraction in a half revolution, the contractions being small compared with the expansions. When the field is rotated through 180° in the (011) plane only one maximum of expansion and one of contraction are obtained.

For the transverse field rotated in these same two planes the magnetostriction at right angles to the field is taken in the plane of rotation. The curves are similar to those for the longitudinal field except that there is an interchanging of contraction and expansion. If a crystallographic axis expands in a longitudinal magnetic field it contracts by about the same amount when turned transverse to the field; or if it contracts in the longitudinal field the transverse field will make it expand by about the same amount.

A number of experiments were made to see whether the magnetostriction perpendicular to a given plane varied with the direction of the field in this plane. The transverse field was found to produce the same expansion of a given tetragonal axis (within the limits of error of the experiment) when directed along one of the perpendicular tetragonal axes as when parallel with one of the perpendicular digonal axes. Ap-

[2] Kunz, Bull. Nat. Res. Council, **3**, 177, 1922

parently, therefore, rotation of the field in the (100) plane does not change the magnitude of the magnetostriction normal to this plane. Further experiments made it seem probable that the magnetostriction normal to the (011) plane and to the (111) plane is unaltered by rotating the field in these respective planes.

Discussion of Results with Reference to Theories

In the previous paper it was suggested that Ewing's recent model of the magnetic atom could be made to fit in with magnetostriction phenomena. The present experiments seem to impose the following conditions on this model in magnetite:

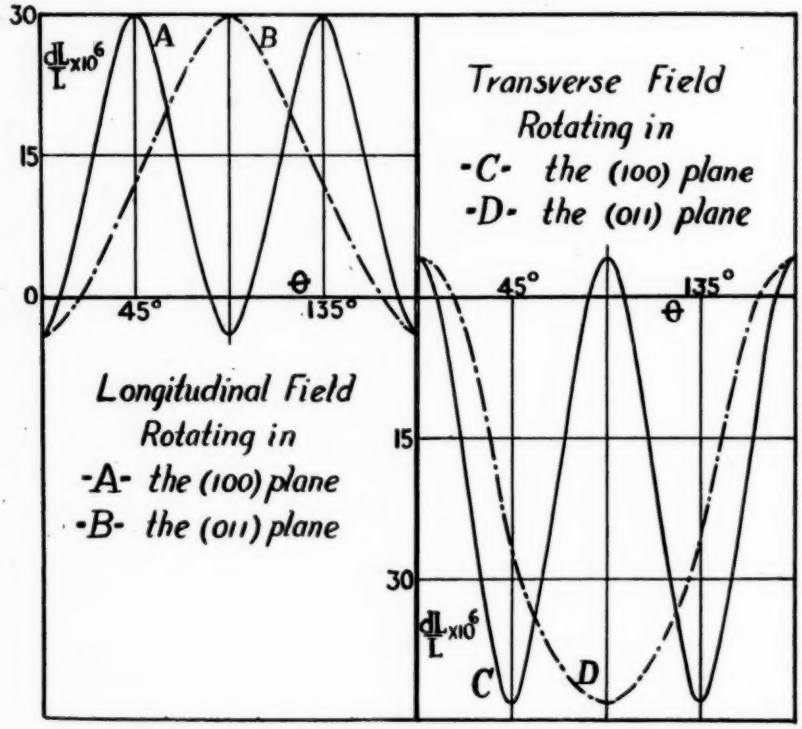

Fig. 3. Magnetostriction for different directions in given planes.

1. In one complete rotation of the Weber element in the (100), (010), or (001) planes it passes through four positions of maximum force which tend to expand the crystal and four positions of maximum force which tend to contract it. This force is presumably exerted by the Weber element either on the outer parts of its own molecule or on neighboring molecules. In the former case it must be supposed that the molecule is

strained and that the straining of the molecules alters the distances between their centers.

2. The Weber element must possess laterally a mechanism for producing the same type of force changes as are produced longitudinally.

3. The Weber element, or the rotating mechanism, must be confined to the inner part of the molecule. Otherwise a magnetic field, by rotating the outer parts of the molecules, could produce changes in those properties of the crystal, such as cohesion, etc., which depend on the outer parts of the molecules, and the crystallogrpahic axes could have their directions changed by means of a magnetic field.

The following modification of Ewing's model will satisfy the above conditions. Let the fixed outer portion of the molecule be represented by a cube with twelve magnets fixed respectively to the center of each edge, the north pole of each magnet being directed inwards and the axes of the magnets being supposed to lie along the digonal axes of the cube. The rotating element may consist of a similar cube centered within the first, the magnets of the inner cube having their south poles directed outwards towards the north poles of the outside cube. An externally applied field must exert a directive influence on this cube; also the longitudinal magnetostrictive effects are the converse of the transverse effects. Hence it is necessary to assume that one pair of magnets, with axes on the same line, have their north poles protruding, and one of these two north poles is slightly stronger than the other.

Fig. 4 gives a diagram of the model. Here the inner rotating cube is considerably simplified for the sake of clearness. Only the magnets are shown, and each of the poles marked Σ is supposed to take the place of four south poles making angles of 60° with each other. The poles of the Weber element in the position shown are supposed to lie very close to the planes of the outer cube in which the north poles are situated. These latter poles are represented by circles. In the diagram, if N' is stronger than N the external field may be supposed directed along Ox.

Magnetostriction can occur as follows: In the position shown each pole marked S will attract those north poles of the plane in which it lies. The two Σ poles will exert attractive forces on all the poles of the external shell, the compressive force being less along the direction Oz than along the other two axes. The poles N and N', lying approximately in the two yOz planes of the diagram, will exert repulsive forces on the north poles of these respective planes. Hence all the forces named tend to produce contraction in the direction of the field, that is, along the tetragonal axis of the crystal. Expansion in transverse directions would

result if the repulsive effects of the N and N' poles exceed the other attracting forces.

It seems probable that the action of the Weber element on similar elements in neighboring molecules should be considered. In this case contraction in the direction of the field would result provided the following condition is satisfied along Ox: compressive force of S poles + compressive force of Σ poles > expansive force of N and N' acting on the N' and N poles of neighboring elements. To produce transverse expansion, along Oz for example, we must have for this direction: compressive force of S poles + compressive force of Σ poles < repulsive force of N and N'+ repulsive force of Σ poles on the Σ poles of neighboring elements. In Fig. 4 the inner system is shown in a position which would not

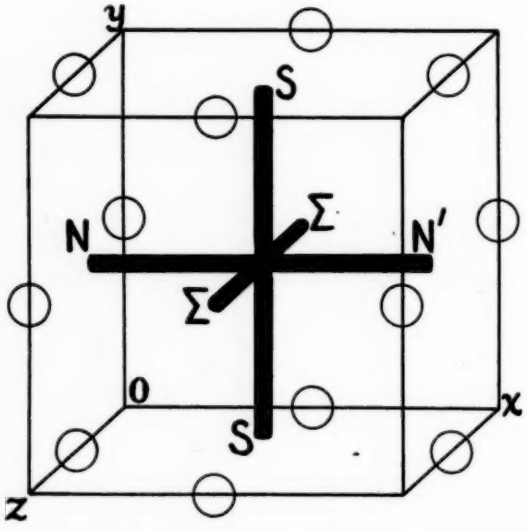

Fig. 4. Model of the magnetic element in magnetite.

be stable when forces exist between the different systems. For stability under these conditions the Weber element must be rotated slightly about the Ox axis. However it is possible in the rotated position to explain magnetostriction in the same way that it is explained above. When the field is directed along the digonal axis of the cube a large expansion in the direction of the field is to be expected and a similar large contraction transverse to the field, because in this case each pole of the Weber element is directly under a pole of the outer shell.

If the influence of neighboring atoms is to be considered in the fashion outlined above it is obviously of importance to know the crystalline

structure of magnetite in detail. W. H. Bragg[3] has analyzed this mineral and found it to have a space lattice similar to that of diamond. The (100) planes consist of Fe_2O_4 planes having the spacing 2.07 A interleaved with Fe planes. The (110) planes consist of Fe_2O_2 planes 2.94 A apart interleaved with FeO_2 planes. The (111) planes are Fe planes 4.8 A apart interleaved with several iron and oxygen planes. On the average it appears that the (110) planes have the largest spacing; it is also these planes which experience the greatest normal displacements under the influence of parallel or normal fields. It is possible that the greater spacing of these planes gives them greater freedom of motion. The weaker forces of the Weber elements on each other across the greater interplanar distance does not appear to be of importance in the model suggested above, since it is assumed practically negligible in this direction.

This model of the magnetic atom of magnetite is to be considered merely as suggestive. When the magnetostriction of a pure iron crystal has been investigated it may be possible, knowing the space lattice of magnetite, to devise a much more satisfactory model. The one suggested, however, agrees with the concentric shell theory of the atom and it meets the demand that the rotating element should be only a small part of the atom. On modern theories of atomic structure the magnets of this model would naturally be replaced by electron orbits. In this case there is objection to the model on theoretical grounds, since for stability it appears that the orbits should be coplanar. It is entirely possible that a Weber element could be devised with parallel magnets and that this element could be made to give the magnetostriction found experimentally. However, the assumptions regarding the nature of the forces do not appear to be simple enough. The approximate equality of the magnitudes of the transverse and longitudinal magnetostrictions suggests similar mechanisms for the production of the effects. It seems natural, therefore, to suppose that if aligned north poles produce longitudinal expansion then south poles aligned in this same direction produce the transverse contraction. Thus magnetostriction phenomena in magnetite favor the view that the magnetic element is a group of electrons rotating in orbits which are not parallel with each other. This group is probably one of the inner shells of the atom.

THE RICE INSTITUTE,
HOUSTON, TEXAS.
February 4, 1924.

[3] W. H. Bragg, Phil. Mag. **30**, 305 (1915)

ELECTROMAGNETIC INDUCTION IN A HOMOGENEOUS SOLID CONDUCTING SPHERE ROTATING ABOUT AN AXIS PERPENDICULAR TO A UNIFORM ALTERNATING MAGNETIC FIELD

By Alexander Marcus

Abstract

(1) *Mathematical theory.* The differential equations of the field are solved by a method first given by H. Lamb. The induced currents are found to flow in concentric shells; to an observer moving with the sphere they would be equivalent to two sets of steady currents revolving in the sphere with frequencies equal respectively to the sum and the difference of the frequencies of the impressed alternating field and of rotation of the sphere. The currents may be supposed to diffuse from the surface inward in the usual manner; at higher frequencies the penetration is smaller, resulting in a "skin effect" for high frequencies. Equations are also derived for the resulting magnetic field and for the torque on the sphere and for the logarithmic decrement in the case of an oscillating conducting sphere. (2) To test the theoretical results, *measurements of the logarithmic decrement of a solid metal ball* oscillating about a vertical axis in an alternating field produced by a long horizontal solenoid were made, and the results for three balls were found to agree with values computed from the theoretical expression for the torque within the limit of experimental error, which was not greater than a few tenths per cent.

THE subject of electromagnetic induction in spherical conductors has been investigated by many writers and the special cases that have been treated thus far may be divided into two classes, dealing either with a sphere at rest in an alternating magnetic field or with a sphere rotating in a steady field. Solutions of these cases have been published by C. Niven,[1] H. Lamb,[2] J. Larmor,[3] J. J. Thomson,[4] H. Hertz,[5] and R. Gans.[6]

So far as the writer is aware, no one has hitherto published the solution of the problem of a sphere rotating in an alternating magnetic field. The general problem of rotation in an oblique field breaks up into two cases, for a magnetic field that is unsymmetrical to the axis of rotation may be resolved into two components, one that is symmetrical to the axis and another that is perpendicular to the axis. The alternating symmetrical component produces the same effect, so far as the currents in

[1] C. Niven, Phil. Trans. part II, 1881
[2] H. Lamb, Phil. Trans. part II, 1883
[3] J. Larmor, Phil. Mag. Jan. 1884
[4] J. J. Thomson, Recent Researches, pp. 546-557
[5] H. Hertz, Collected Papers
[6] R. Gans, Zeit. f. Math. und Physik, **48**, No. 1, 1902

the sphere are concerned, whether the sphere be stationary or rotating, for the number of lines of magnetic force that thread through any closed curve in the sphere remains unchanged by the rotation. We shall therefore proceed directly to the case of rotation in the magnetic field that is perpendicular to the axis.

Let us suppose that the sphere is rotating with constant angular velocity ω about the Z axis in an alternating field $H \cos pt$ parallel to the X axis. In this case the induced currents and the magnetic field are exactly the same as they would be in a stationary sphere placed in an alternating field revolving with angular velocity $-\omega$, referred to a set of axes X, Y, Z fixed relative to the apparatus producing the field. The components of the latter are derivable from the potential $Hx \cos pt$. As we shall use spherical coordinates throughout this paper we may write this expression as $Hr \sin \theta \cos \varphi \cos pt$. As viewed by an observer moving with the sphere, the impressed field is given by the gradient of $Hr \sin \theta \cos (\varphi_0+\omega t) \cos pt$, since the only coordinate that is influenced by the motion is φ and the relation between φ and φ_0 is given by $\varphi=\varphi_0+\omega t$ where φ_0 pertains to the system of axes revolving with the sphere.

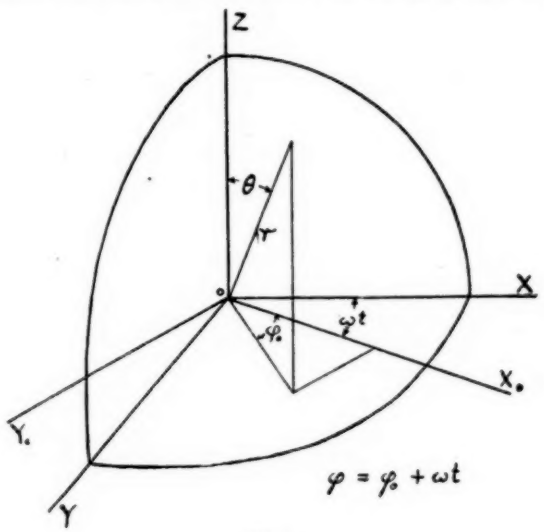

Fig. 1

Mathematically the problem is now reduced to the case of a stationary sphere in an alternating field whose components with respect to the r, θ and φ_0 coordinates are $[H \sin \theta \cos pt \cos (\varphi_0+\omega t)]_r$, $[H \cos \theta \cos pt \cos (\varphi_0+\omega t)]_\theta$, and $-[H \cos pt \sin (\varphi_0+\omega t)]_\varphi$ or $\{\frac{1}{2}H \sin \theta \cos [\varphi_0+(\omega+p)t] + \frac{1}{2}H \sin \theta \cos [\varphi_0+(\omega-p)t]\}_r$ etc. To find the induced effects we may now employ Maxwell's equations for stationary medja. The following

symbols will be used in the equations: M, the resultant magnetic intensivity: E, the resultant electric intensity; r,θ,φ_0 the polar coordinates of a point; c, the velocity of light; λ, the conductivity of the metal; a, the radius of the sphere; n, the frequency of the currents in the primary coil; m, the frequency of rotation of the sphere. M and E are both measured in electromagnetic units.

The equations pertaining to a particle within the sphere are

$$\text{curl } M = 4\pi\lambda E; \tag{1}$$

$$\text{curl } E = dM/dt; \tag{2}$$

$$\text{div } E = 0 = \text{div } M; \tag{3}$$

$$\nabla^2 M = 4\pi\lambda dM/dt; \tag{4}$$

$$\nabla^2 E = 4\pi\lambda dE/dt. \tag{5}$$

As we may neglect the displacement currents in this case, we get for the region outside of the conductor the equations $\nabla^2 M = 0$ and $\nabla^2 E = 0$.

The impressed field gives rise to two types of electromagnetic disturbances, the free or transient vibrations and the forced vibrations. If we allow sufficient time for the free disturbance to subside, we need concern ourselves only with the forced vibrations. Moreover the problem of determining the precise mode in which the transient effects are dissipated in time and space in a stationary sphere has been completely solved by H. Lamb.[7] His solution will apply directly to the case of a revolving sphere, for as regards the transient effects the frequency of the impressed field is of no importance and as we have replaced the motion of the sphere by an appropriate variation of the impressed field, angular velocity of the sphere also can not influence the transients.

The part of the problem which has not been solved heretofore is based on the solution of the equation of the type $\nabla^2 M = 4\pi\lambda dM/dt$ which will also satisfy $\text{div } M = 0$ as well as the boundary conditions. We have already proved that relative to the rotor, the impressed field has two frequencies proportional to $p+\omega$ and $\omega - p$ respectively, where $p = 2\pi n$ and $\omega = 2\pi m$. We may therefore assume that M and E vary as ϵ^{qt} where $q = (\omega \pm p)j$ where $j = \sqrt{-1}$ and $k^2 = 4\pi\lambda q$. Eq. (4) may now be put into the form:[8]

$$\text{(I)} \quad \frac{\partial^2(r^2 M_r)}{r^2 \partial r^2} + \frac{\partial(\sin\theta\, \partial M_r/\partial\theta)}{r^2 \sin\theta\, \partial\theta} + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2 M_r}{\partial\varphi^2} + k^2 M_r = 0,$$

with two similar expressions in M_θ and M_φ, and $\text{div } M = 0$ may be expanded into

$$\text{(II)} \quad \frac{1}{r^2} \frac{\partial}{\partial r} r^2 M_r + \frac{1}{r \sin\theta} \frac{\partial}{\partial\theta} \sin\theta\, M_\theta + \frac{1}{r \sin\theta} \frac{\partial M_\varphi}{\partial\varphi} = 0.$$

[7] Lamb, Phil. Trans., part II, 1883

[8] H. Weber, Die Part. Diff. Gleich., pp. 336-337.

Lamb has long ago given two particular solutions of the systems (I) and (II) but only one of these solutions is appropriate to our problem. Bromwich[9] has recently proved that the general solution of Maxwell's equations can be derived by superposing two special solutions which can be obtained by taking first $E_r=0$ and secondly $M_r=0$. These two solutions are of a reciprocal character and when $E_r=0$ none of the components of M can vanish, while if $M_r=0$ none of the components of E can vanish. It is obvious that the particular solution which makes $M_r=0$ is inapplicable to this case.

The appropriate form of the solution is

$$\left.\begin{aligned} M_r &= -\sum_1^2 6f_1(k_n r)\frac{S_n}{r}\epsilon^{q_n t};\\ M_\theta &= \sum_1^2 \left\{2f_0(k_n r)-k^2r^2f_2(k_n r)\right\}\frac{1}{r}\frac{\partial S_n}{\partial\theta}\epsilon^{q_n t};\\ M_\varphi &= \sum_1^2 \left\{2f_0(k_n r)-k^2r^2f_2(k_n r)\right\}\frac{1}{r\sin\theta}\frac{\partial S_n}{\partial\varphi_0}\epsilon^{q_n t}; \end{aligned}\right\} \tag{6}$$

$$\left.\begin{aligned} E_r &= 0;\\ E_\theta &= -\sum_1^2 \frac{3q}{\sin\theta}f_1(k_n r)\frac{\partial S_n}{\partial\varphi_0}\epsilon^{q_n t};\\ E_\varphi &= \sum_1^2 3qf_1(k_n r)\frac{\partial S_n}{\partial\theta}\epsilon^{q_n t}. \end{aligned}\right\} \tag{7}$$

$S_n=A_n r\sin\theta\,\epsilon^{j\varphi_0}$, where A is a constant. $f_0(k_n r)$, $f_1(k_n r)$, and $f_2(k_n r)$ all satisfy

$$\frac{d^2f_n}{dx^2}+\frac{2(n+1)}{x}\frac{df_n}{dx}+f_n=0,$$

where

$x=k_n r$, $k_1=\frac{1}{2}\sqrt{2}\,(1+j)\sqrt{4\pi\lambda(\omega+p)}$, and $k_2=\frac{1}{2}\sqrt{2}\,(1+j)\sqrt{4\pi\lambda(\omega-p)}$

and

$$q_1=j(\omega+p) \text{ and } q_2=j(\omega-p).$$

Eqs. (6) and (7) were obtained from the corresponding expressions in Cartesian coordinates given by Lamb in his third edition of "Hydrodynamics" on pages 572-573. The differential equation in f_n corresponds to Lamb's differential equation in R_n on page 478 of the Hydrodynamics. It is necessary to use the following recurrence relations between f_0, f_1 and f_2 in order to make (6) and (7) satisfy the field equations

$$f_{n+1}(x)=-\frac{1}{x}\frac{df_n(x)}{dx}, \text{ and } x\frac{df_n}{dx}+(2n+1)f_n=f_{n-1}.$$

[9] Bromwich, Phil. Mag. (July 1919)

Since $\nabla^2 M = 0$ outside of the sphere, the magnetic intensity due to the currents is derivable from a potential. We may therefore write for this part of the field

$$\left.\begin{aligned} M_r' &= -\sum_1^2 a^3 \frac{\partial}{\partial r}\left(\frac{\chi_n}{r^3}\right)\epsilon^{q_n t}; \\ M_\theta' &= -\sum_1^2 a^3 \frac{\partial}{r\partial\theta}\left(\frac{\chi_n}{r}\right)\epsilon^{q_n t}; \\ M_\varphi' &= -\sum_1^2 a^3 \frac{\partial}{r\sin\theta\,\partial\varphi}\left(\frac{\chi_n}{r^3}\right)\epsilon^{q_n t}; \end{aligned}\right\} \tag{8}$$

where $\chi = B_n r \sin\theta\, \epsilon^{j\varphi_0}$.

In order to find the A_n's and B_n's in (6), (7), and (8) we apply the boundary conditions for M. The tangential components of M on both sides of the surface of the sphere are equal, and since the permeability of the metal is 1, we may also equate the radial components of M on both sides of the boundary. These two conditions give us a pair of simultaneous equations in the A_n's and B_n's corresponding to each of the two frequencies.

At $r = a$

$$-6f_1(k_1a)A_1 \sin\theta\,\epsilon^{j\varphi_0}\epsilon^{j(p+\omega)t} = 2B_1 \sin\theta\,\epsilon^{j\varphi_0}\epsilon^{j(p+\omega)t} + \tfrac{1}{2}H\sin\theta\,\epsilon^{j\varphi_0}\epsilon^{j(p+\omega)t},$$

and

$$[2f_0(k_1a) - k^2a^2f_2(k_1a)]A_1\cos\theta\,\epsilon^{j\varphi_0}\epsilon^{j(p+\omega)t} = -B_1\cos\theta\,\epsilon^{j\varphi_0}\epsilon^{j(p+\omega)t} + \tfrac{1}{2}H\cos\theta\,\epsilon^{j\varphi_0}\epsilon^{j(p+\omega)t}$$

with two similar equations connecting A_2 with B_2. The terms in H on the right represent the impressed field. Therefore

(a) $6f_1(k_1a)A_1 + 2B_1 = -\tfrac{1}{2}H$;

(b) $[2f_0(k_1a) - k^2a^2f_2(k_1a)]A_1 + B_1 = \tfrac{1}{2}H$;

but $3f_1(k_1a) = -f_0(k_1a) - k_1^2a^2f_2(k_1a)$, and substituting for $k_1^2a^2f_2(k_1a)$ in (b) we get

(c) $3[f_0(k_1a) + f_1(k_1a)]A_1 + B_1 = \tfrac{1}{2}H$.

From (a) and (b) we find

$$A_1 = \frac{H}{4f_0(k_1a)}, \quad \text{and} \quad B_1 = \frac{-H[3f_1(k_1a) + f_0(k_1a)]}{4f_0(k_1a)}.$$

Similarly we find

$$A_2 = \frac{H}{4f_0(k_2a)}, \quad \text{and} \quad B_2 = \frac{-H[3f_1(k_2a) + f_0(k_2a)]}{4f_0(k_2a)}.$$

The value of M due to the currents and the value of E are now given by the real components of the following expressions for space inside:

$$\left.\begin{aligned} M_r &= -\frac{3}{2}H\sin\theta\left\{\frac{f_1(k_1r)}{f_0(k_1a)}\epsilon^{j[\varphi_0+(p+\omega)t]}+\frac{f_1(k_2r)}{f_0(k_2a)}\epsilon^{j[\varphi_0+(\omega-p)t]}\right\} \\ M_\theta &= \frac{3}{4}H\cos\theta\left\{\frac{f_0(k_1r)+f_1(k_1r)}{f_0(k_1a)}\epsilon^{j[\varphi_0+(p+\omega)t]}+\frac{f_0(k_2r)+f_1(k_2r)}{f_0(k_2a)}\epsilon^{j[\varphi_0+]\omega-p[t]}\right\} \\ M_\varphi &= -\frac{3}{4}jH\left\{\frac{f_0(k_1r)+f_1(k_1r)}{f_0(k_1a)}\epsilon^{j[\varphi_0+(p+\omega)t]}+\frac{f_0(k_2r)+f_1(k_2r)}{f_0(k_2a)}\epsilon^{j[\varphi_0+(\omega-p)t]}\right\}. \end{aligned}\right\} \quad (9)$$

$$\left.\begin{aligned} E_\varphi &= -j\frac{3}{4}Hr\cos\theta\left\{(\omega+p)\frac{f_1(k_1r)}{f_0(k_1a)}\epsilon^{j[\varphi_0+(p+\omega)t]}+(\omega-p)\frac{f_1(k_2r)}{f_0(k_2a)}\epsilon^{j[\varphi_0+(\omega-p)t]}\right\} \\ E_\theta &= \frac{3}{4}Hr\left\{(\omega+p)\frac{f_1(k_1r)}{f_0(k_1a)}\epsilon^{j[\varphi_0+(p+\omega)t]}+(\omega-p)\frac{f_1(k_2r)}{f_0(k_2a)}\epsilon^{j[\varphi_0+(\omega-p)t]}\right\}. \end{aligned}\right\} \quad (10)$$

$f_0(x)$ may have any of the forms $\sin x/x$, $\cos x/x$, ϵ^{jx}/x, and $f_1(x)$ may have any of the forms

$$-\frac{1}{x}\frac{d}{dx}\frac{\sin x}{x},\quad -\frac{1}{x}\frac{d}{dx}\frac{\cos x}{x},\quad -\frac{1}{x}\frac{d}{dx}\frac{\epsilon^{jx}}{x}$$

The only form of $f_1(x)$ which is applicable to space inside, where x may become 0, is the first, and at $x=0$, $f_1(x)=1/3$.

The two cases of interest are first the one in which p and ω are small and ka small, and second, the one in which p and ω are large and ka large.

For small values of x, $f_0(x)=1$ (approx.), $f_1(x)=1/3$.

For large values of x, $f_0(x)=\epsilon^{jx}/2jx$, $\quad f_1(x)=\epsilon^{jx}/2x^2$.

Substituting in the general formulas (9) and (10), we get for kr small, inside:

$$E_\theta=\tfrac{1}{4}Hr\{(\omega+p)\cos[\varphi_0+(\omega+p)t]+(\omega-p)\cos[\varphi_0+(\omega-p)t]\} \quad (11)$$

etc.

$$M_r=-\tfrac{1}{2}H\sin\theta\{\cos[\varphi_0+(\omega+p)t]+\cos[\varphi_0+(\omega-p)t]\} \quad (12)$$

etc. For large values of kr inside, we must take the real parts of the following expressions:

$$E_\theta=\frac{3}{8\sqrt{\pi}}\frac{a}{r}\left\{\sqrt{\frac{p+\omega}{\lambda}}\epsilon^{-m_1(a-r)-j[m_1(a-r)+\pi/4]}\epsilon^{j[\varphi_0+(p+\omega)t]}+\sqrt{\frac{\omega-p}{\lambda}}\epsilon^{-m_2(a-r)-j[m_2(a-r)+\pi/4]}\epsilon^{j[\varphi_0+(\omega-p)t]}\right\} \quad (13)$$

$$M_r = -\frac{3H}{4\sqrt{\pi}}\frac{a}{r^2}\sin\theta\left\{\frac{\epsilon^{-m_1(a-r)-jm_1(a-r)}}{\sqrt{\lambda(\omega+p)}}\cos[\varphi_0+(\omega+p)t]\right.$$
$$\left.+\frac{\epsilon^{-m_2(a-r)-jm_2(a-r)}}{\sqrt{\lambda(\omega-p)}}\cos[\varphi_0+(\omega-p)t]\right\} \quad (14)$$

$m_1=\sqrt{2\pi\lambda(\omega+p)}$, $m_2=\sqrt{2\pi\lambda(\omega-p)}$ or $\sqrt{2\pi\lambda(p-\omega)}$ according as $p<\omega$, or $p>\omega$.

From the expressions for M and E it follows that an observer moving with the sphere will detect a pair of revolving fields and two sets of revolving currents.

Let us now consider the penetration of the disturbance within the solid. For small values of p and ω the current density on any shell varies directly as the radius of the shell, being a maximum at the surface and zero at the center. The impressed magnetic field being uniform, the same inductive effect is produced on all concentric shells.

For p and ω large, the penetration within the conductor takes place as a propagation of two highly damped waves inward from the surface. At the surface, the current density increases with the conductivity of the material, for the components of the current density λE vary as $\sqrt{\lambda(\omega\pm p)}$. At any depth $a-r$ beneath the surface, the current density decreases with an increase in λ owing to the very rapid decrease in $\epsilon^{-\sqrt{2\pi\lambda(\omega\pm p)}}$. The surface of a good conductor therefore screens the interior against rapidly varying external electromagnetic disturbances irrespective of whether the induced effects be due to the rotation of the conductor or the variation of the field or to the two combined. In the case of a conductor rotating in a field that is not symmetrical to the axis of rotation the surface can shield the interior only against non-symmetrical components, for the rotation in the symmetrical field is not accompanied by induced currents. These facts lead to the view that the direct induction creates only superficial currents at the start. These currents, were there no resistance, would continue to flow undiminished and would prevent the interior of the solid from being affected. The sphere may be regarded as made up of an infinite number of conducting shells. As the currents of the outer shell decay by resistance this shell ceases to be a complete screen. Currents are then created in the inner shells by direct induction exactly as in the outer one, and thus the whole sphere becomes pervaded.

The Mechanical Reaction Between the Currents in the Sphere and the Impressed Magnetic Field

If F be the mechanical force per unit volume, then (Maxwell's Treatise, vol. II, §603), $F=[c\times M]$, the right hand member being the vector

product of the impressed magnetic field alone (since the rotor does not produce a torque on itself), and the current at the point in question. Let X, Y, Z, a, b, c, u, v, w be the components of F, M and C along the x_0, y_0 and z axes in the moving system. Then

$$F=\begin{vmatrix} i & j & k \\ u & v & w \\ a & b & c \end{vmatrix}$$

and the couple per unit volume is equal to

$$[r\times F]=\begin{vmatrix} i & j & k \\ x_0 & y_0 & z \\ X & Y & Z \end{vmatrix}$$

where $r=x_0i+y_0j+zk$. The couple around the axis of z is $\iiint(x_0Y-y_0X)\,dx\,dy\,dz$; but $X=bw-cv$ and $Y=cu-aw$. Substituting we get, $y_0X-x_0Y=by_0w-cy_0v-cx_0u+ax_0w=(ax_0+by_0+cz)\,\omega-c(ux_0+vy_0+wz)$. Since $E_r=0$, $wz+vy_0+ux_0=0$, also $ax_0\times by_0+cz=rM_r$ and $\omega=\lambda E_\theta\sin\theta$; hence the torque around the z axis is $\iiint\lambda E_\theta M_r r\sin\theta\,dS$ where $dS=r^2\sin\theta\,d\theta\,d\varphi\,dr$ or

$$\text{Torque}=\int_{r=0}^{r=a}\int_{\theta=0}^{\theta=\pi}\int_{\varphi=0}^{\varphi=2\pi}\lambda E\theta\,M_r\,r^3\sin^2\theta\,d\theta\,d\varphi\,dr. \quad (15)$$

Inserting for M_r only the external field, we find for the average resultant torque

$$\mathcal{J}=\pi\lambda H^2\left\{(\omega+p)\int_0^a\frac{f_1(k_1r)}{f_0(k_1a)}r^4dr+(\omega-p)\int_0^a\frac{f_1(k_2r)}{f_0(k_2a)}r^4dr\right\} \quad (16)$$

For p and ω small,

$$\frac{f_1(k_1r)}{f_0(k_1a)}=\frac{f_1(k_2r)}{f_0(k_2a)}=\frac{1}{3},$$

hence the resultant torque is

$$\mathcal{J}=\tfrac{2}{15}\pi a^5\lambda H^2\omega. \quad (17)$$

In so far as the reaction upon the impressed field is concerned, the currents in the sphere flow as though they were confined to tubes coinciding with great circles through the axis of rotation, for in the expression for the torque the only component of the current that appears is E_θ. Moreover if we calculate the line integral of $E\varphi$ about a line whose plane is perpendicular to the axis of rotation we find that it vanishes, i.e.

$$\int_0^{2\pi}E\varphi a\sin\theta\,d\varphi_0=0.$$

This must necessarily be true since there is no impressed field parallel to the axis of rotation.

Experimental Confirmation

The foregoing theoretical development was tested experimentally in the following manner. A metal ball was suspended by means of a torsion fibre at the center of a long solenoid carrying a steady alternating current. The suspension fibre was perpendicular to the direction of the field. The ball was given a start and allowed to oscillate freely in air, and an observation of the decrement of the oscillation was taken. The field was then thrown on and the decrement was again determined. The difference between the two decrements gave the component due to the induced currents alone. The latter could be predetermined from theory as follows.

The equation of motion of the ball is given by

$$P\frac{d^2\varphi}{dt^2}+k\frac{d\varphi}{dt}+\tau\varphi=0 \tag{18}$$

where P is the moment of inertia and k the coefficient of damping including air damping as well as electromagnetic damping. τ is the restoring moment for unit angular deflection of the elastic suspension fibre. The solution of (18) is given by

$$\varphi=\varphi_0\epsilon^{-kt/2P}\cos\,(2\pi t/T) \tag{19}$$

where T is the period.

If δ be the logarithmic decrement of the oscillation we can prove by means of (19) that $\delta=kT/4P$.

In the experiments the period of oscillation of the ball ranged from about four to fifteen seconds; therefore it was permissible to compute the theoretical value of δ on the assumption that the angular velocity ω was constant at any time.

The first experimental test was performed to check the result given by (17) for the average resultant torque. This expression for $\mathcal{T}$ should be strictly true, according to the theory, for impressed fields of zero frequency. Accordingly, metal balls having different resistivities were suspended in turn in uniform constant magnetic fields and allowed to oscillate. The damping due to the induced currents was measured in each case and the logarithmic decrement for each ball was compared with the value given by the theoretical expression. The latter is found in the following manner. $\delta=kT/4P$ where $k=\mathcal{T}\omega$ and, for a sphere, $P=\frac{2}{5}a^2M$; hence $\delta=TH^2\pi a^3/12M\sigma$, where σ is the resistivity of the material or $1/\lambda$.

In every case the values of δ (the decrement) as given by theory and experiment differed by not more than one tenth of one per cent. This method was later employed to determine σ for copper and for lead from the values of δ obtained experimentally. The values of σ obtained from

the formula agreed with the published values as closely as the different published values agreed among themselves.

The test of the theory was then extended to those cases for which the expression for δ could be put into the form of a rapidly converging power series in the variable $v=2\pi a\sqrt{f/\sigma}$ where a is the radius of the ball and f the impressed frequency. The reason for thus restricting the test was that the separation of the real and the imaginary parts of the integral of (16) becomes extremely laborious except when we restrict the investigation to cases for which $v<\pi$. In the latter cases the expansion is made as follows:

$$\int_0^a \frac{f_1(k_n r)}{f_0(k_n a)} r^4 dr = \frac{a^5}{x^2}\left[1+\frac{3\cot x}{x}-\frac{3}{x^2}\right]$$

where $x=k_n a$; but

$$\cot x=\frac{1}{x}-\frac{x}{3}-\frac{x^3}{45}-\frac{2x^5}{945}-\frac{x^7}{4725}.$$

On substituting in (16) and changing the variable x into v by the relation $v=2\pi a\sqrt{f/\sigma}$ we get

$$\mathcal{T}=\tfrac{2}{15}(H^2\pi a^5/\sigma)(1-0.1143v^4-7.73\times10^{-3}v^8\ldots)\omega,$$

and

$$\delta=(TH^2\pi a^3/12M\sigma)(1-0.1143v^4-7.73\times10^{-3}v^8\ldots).$$

Apparatus

The ball was suspended with its center in the middle of a solenoid 122.4 cm long having an average diameter of 7.1 cm. The solenoid consisted of two separate but identical parts each wound with four layers of No. 16 cotton-covered copper wire. The ball was suspended by means of a phosphor-bronze ribbon within a box mounted on leveling screws. When the solenoids were placed in contact over the ball the two end turns touched at nearly all points. There was a very narrow short slit at the top to allow the suspension to pass through. Readings of successive amplitudes were taken by observing the deflection of a beam of light on a scale about a meter away.

Balls of different non-magnetic metals were used. The frequencies of the impressed field ranged from zero to 580 cycles per second. In every case it was necessary to determine the resistivity of the sample of metal used. This was done by keeping the field constant and measuring the decrement. The resistivity was computed from $\delta_0=TH^2\pi a^3/12M\sigma$. This expression for δ_0 follows directly from our theoretical expression for δ_0 in an alternating field by putting $f=0$.

TABLE I

Comparison of experimental and theoretical values of the decrement ρ.

Substance	a	M	T	i (effective)	f	ρ (exp.)	ρ (theor.)
Copper	0.96 cm	33.76 g	14.9 sec.	1.66 amp.	64.7	1.135	1.133
Copper	0.53	5.86	4.62	4.00	580	1.013	1.013
Lead	1.17	79.86	5.24	3.17	62	1.003	1.003

The effective value of H in the expression for δ is given by $H=30.308i$ where i is in (effective) amperes.

In each case the experimental value of ρ is the mean of a large number of observations and the probable error of the mean was in no case greater than one part in a thousand. The maximum deviation of a single observation from the mean was about five parts in a thousand.

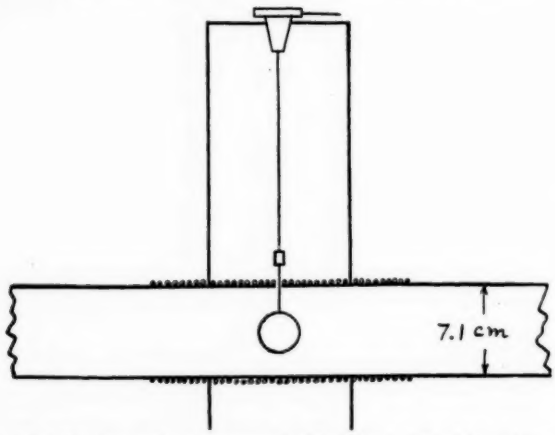

Fig. 2. Oscillating sphere suspended inside a solenoid, 122 cm long.

A comparison of the values of ρ as found experimentally with those computed from the theory shows that within the limits of experimental error, theory and experiment give the same values.

In closing the writer wishes to acknowledge the fact that Prof. M. I. Pupin suggested the investigation and that he is particularly indebted to Prof. A. P. Wills for a number of helpful criticisms.

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THE RATE OF EVAPORATION OF LIQUIDS IN A CURRENT OF AIR[1]

By T. B. Hine

Abstract

The experiments were made in a large ventilating tunnel at Edgewood Arsenal near the end of a 280 ft straight section, 6 ft square. The liquid being studied was pumped continuously into a copper pan mounted flush with the floor, over the edge of which it overflowed into a lower pan. The amount of evaporation in several hours was determined by weighing the pans. Results were obtained for *chlorbenzene, M-xylene, nitrobenzene and toluene, for winds from 0 to 15 miles per hr*, 49 runs in all. The rate of evaporation is found to be a linear function of the wind velocity, and taking the values of vapor pressure given in the literature corresponding to the temperatures of the liquid surfaces, the relation suggested by DeHeen in 1891 is found to be correct; the number of gram mols evaporated per hour from a liquid surface 60 cm in diam. is given by $M=(0.1+0.10W)P$, where W is the wind velocity in miles per hour and P is the vapor pressure in millimeters of mercury. Due to variations in the wind velocity and uncertainty as to the exact temperature of the surface in some cases, the mean variation of observed values of M from the computed values is about 10 per cent, but there is no evidence of a systematic deviation of the results for any one liquid, although the vapor pressures very from 0.3 to 30 mm.

I. Introduction

THE persistence of a chemical warfare agent in the field is mainly determined by its rate of evaporation under the conditions of distribution employed. If we know the persistence of one substance for a given mode of distribution, and the relation between the physical properties of a substance and its rate of evaporation, we should be able to predict the persistence of a new substance, and perhaps gain an approximate idea of the concentrations in the air over an evaporating area. For this reason, the following study of the laws of evaporation was undertaken.

II. Historical and Theoretical

The importance of water evaporation phenomena for the agriculturist, engineer, and meteorologist has resulted in many investigations and the collection of a considerable mass of data, but unfortunately the greater bulk of the literature is concerned with the statistics of evaporation, and is not of immediate value in determining the physical laws of evaporation. Another difficulty that we encounter in analyzing much of the data of water evaporation is that the rate of evaporation is very dependent upon the humidity of the air which is seldom measured very accurately and

[1] A contribution from the Chemical Warfare Service, War Department.

which is subject to rather rapid and irregular changes, thus introducing an uncertainty that necessitates a very cautious use of the conclusions based on water evaporation in our study of the rate of evaporation of other liquids.

There is no comprehensive and critical treatise on this subject, but fortunately, the several hundred widely scattered publications up to the year 1909 have been covered in an excellent annotated bibliography by Mrs. Grace L. Livingston,[2] and the literature since that date may be readily found in the abstract journals. An inspection of this voluminous literature reveals the rather surprising fact that almost no work has been done with liquids other than water and that very few experiments have been sufficiently controlled to indicate the effect of each of the factors that together determine the rate of evaporation of a liquid in a current of air.

There have been a number of empirical formulas proposed to express the rate of evaporation of water, but there is none that has proved sufficiently satisfactory to be generally adopted, and they have not been tested in their application to liquids other than water.

Since John Dalton[3] nearly all investigators have agreed that the rate of evaporation of water is proportional to the saturation deficiency. This may be expressed as the difference between the vapor pressure of the water at the temperature of the water and the partial pressure of water vapor in the air. The partial pressure of water vapor in the air (or the absolute humidity) is generally determined at a great distance from the surface, or before the air passes over the water surface whose evaporation is being considered. Apparently assuming that the temperature of an evaporating water surface would be the same as that of a wet bulb thermometer, certain writers following Tate[4] have expressed the rate of evaporation as proportional to the depression of the wet bulb below the dry bulb thermometer. With the above assumption this would follow from the ordinary psychometric relation that the difference between the tension of saturated vapor at the temperature of the wet bulb and the actual tension of vapor present in the air at the temperature of the dry bulb is proportional to the depression of the wet bulb reading below the dry bulb reading. Aside from the undesirability of introducing into a physical relation factors dependent upon apparatus construction and operation, the main objection to setting the rate of evaporation

[2] Mrs. Grace L. Livingston, Monthly Weather Review, June, September, November, 1908, and February, March, April, May and June, 1909

[3] John Dalton, Mem. Lit. Phil. Soc. **5**, 535-602 (1802)

[4] Thomas Tate, Phil. Mag. **23**, pp. 126, 283, 494 (1862); **25**, 331 (1863)

proportional to the psychrometric difference is that it takes no account of the temperature of the evaporating liquid which may be very different from that of a ventilated wet bulb.

In considering the rate of evaporation of liquids other than water the air in most cases will not contain any of the vapor of the evaporating liquid before passing over its surface or at a considerable distance above the surface, and consequently we shall not be troubled by the fluctuations in humidity which so profoundly influence the rate of evaporation of water in the open. For any given liquid evaporating into air previously devoid of its vapor we might expect that, with the other factors constant, the weight evaporated per unit time would be proportional to the vapor pressure at the temperature of the liquid. This is equivalent to considering that the same volume of air saturated with vapor is removed per unit time with other factors constant, since the weight of a substance in a given volume of saturated air is, of course, proportional to the vapor pressure of the substance. If we now wish to compare the rate of evaporation of different liquids under otherwise constant conditions, we might expect the same volume of saturated air to be removed per unit time in each case, and, of course, the weight of substance contained in this volume in each case is proportional to the vapor pressure and the molecular weight of the substance. As a result of experiments on the rate of evaporation of liquids from a bottle in a current of air, DeHeen[5] concluded that the weight evaporated per unit time is proportional to the product of the molecular weight by the vapor pressure. This may be expressed in another way by saying that the number of mols of liquid evaporated per unit time is proportional to its vapor pressure.

It was for the purpose of testing this relationship in the case of a free liquid surface in a horizontal current of air that the experimental work described in the rest of this report was undertaken. We may anticipate the results of this experimental work, and state that within the experimental error we found the relationship correct; the number of mols of a liquid evaporated per unit time from a given surface is proportional to the vapor pressure of the liquid and also to the wind velocity.

III. Experimental[6]

Ventilating Tunnel and Apparatus Used in Evaporating Experiments

In order to have the wind velocity under control, the evaporation experiments were all conducted in one of the large ventilating tunnels

[5] P. DeHeen, Bul. Acad. Sci. de Belgique, **21**, 11-25, 214-9, 798-810 (1891)

[6] Most of the experimental work here described was performed by Mr. D. Clark with general supervision by the author.

available at Edgewood Arsenal. The tunnel proper is about 600 feet long and parallel with the ground level. It is constructed of wood double-walled, with a layer of tar paper between, and painted with asphaltum paint. It contains four right-angle bends and is ventilated by four fans, driven by four 20 hp a.c. motors, single speed, which give an air velocity varying from one mile or less, by the use of swinging gates, up to 40 miles per hour, with all fans going and all the control gates open. A low wind velocity can readily be obtained that is constant to within about 1/2 mile per hour. More constant velocities cannot be obtained because outside weather conditions are a controlling factor. The apparatus was set up in a straight section of the tunnel about 280 feet in length with cross section 6 feet square. The wind had a straight sweep of 250 feet before striking the exposed pan containing the evaporating liquid.

The liquids were evaporated in a circular copper pan, 59.06 cm in diameter by 1 cm deep, and were pumped continuously into this pan from which they overflowed the edge into a larger pan containing the bulk of the evaporating liquid. A small pump kept the liquid circulated from the lower to the upper pan at a speed which kept the upper pan overflowing continuously, insuring a full surface of liquid to the wind at all times. The lower pan receiving the overflow was larger in diameter by 5 cm and was not exposed to the effect of the wind. A circular hole 27 inches in diameter, was cut in the floor of the tunnel. A steel plate, 30 inches square, 1/4 inch thick, containing a circular hole cut slightly larger than the diameter of the upper pan but smaller than the diameter of the lower one, was placed over the hole and fastened to the floor. This brought the edge of the upper pan flush with the surface of the steel plate when in position for evaporating. The edge of the lower pan rested firmly against a double gasket of hard and soft rubber on the under side of the steel plate. This insured an air-tight fit between the lower pan and the steel plate.

The small circulating pump was made of aluminum, eccentric type with brass blades, which delivered about 10 cc per minute. The shaft speed was 96 r.p.m. driven from a counter-shaft by a small electric motor, belt connected. The liquid was discharged just above the evaporating surface; it could then be noticed if the pump was functioning properly. The driving apparatus, including the under side of the pan, was housed directly under the tunnel in a suitable manner. The pan was lowered and raised to the tunnel floor by a rope connected to the center of the pan by a hook. The other end of the rope extended over two pulleys and down under the tunnel to a counterweight. This arrangement was

found to be most convenient in lowering and raising the pan without spilling the contents.

A Troemner solution balance No. 80 was used for all weighings of the pan after run No. 12. Before this, several types of balances were tried but the Troemner solution balance No. 80 was found to be the most satisfactory. It was of 20 kg capacity and, when tested for sensitiveness at full load of 8 kg, responded to two grams in each case. In our calculations we have assumed ± 4 grams to be the nearest that the beam could be read in actual work.

The Liquids Used in Evaporation and Their Vapor Pressures

The liquids available in sufficient quantities for these experiments were as follows: toluene, chlorbenzene, m-zylene, nitro-benzene. All were of good quality, but they were purified by us before being used for evaporation.

Toluene (mol. wt. = 92.1) was freed from water with fused calcium chloride and used without further purification. Its boiling point was constant at 110° C and it was considered high grade material pure enough for our purpose.

The vapor pressure at the temperature of the evaporation experiments was calculated from the experimental data of Kahlbaum,[7] Barker,[8] and F. Neubeck[9] by the Kirchoff-Rankine-Dupre formula, $\log P = -A/T - B \log T + C$, where P is the vapor pressure, T the absolute temperature and A, B, and C are constants.

The constants of the equation were evaluated from the pressures given by Kahlbaum for temperatures 298.8°, 304.6° and 318.2° K. The equation used was: $\log P = -2075/T - 0.9286 \log T + 10.7208$. Vapor pressures calculated from this equation agreed satisfactorily with the measured values of Barker and Neubeck, for temperatures 273°, 287.8°, 334.2° and 336.2° K.

Chlorbenzene (mol. wt. = 112.53). This was freed from water with fused calcium chloride and subjected to fractional distillation through a Hempel column containing glass beads, to determine its boiling range only. From a total of 500 cc, 465 cc distilled over between 131° and 132° C and 35 cc came over between 132 and 134° C using a calibrated Anschutz thermometer. This means 93 per cent distilling between the range of 131°-132° C. The boiling point is given in the literature[10] as 131.7°C at

[7] Kahlbaum, Zeit. Phys. Chemie, **26**, 603 (1898)
[8] Barker, Zeit. Phys. Chemie, **71**, 235 (1910)
[9] F. Neubeck, Zeit. Phys. Chemie, **1**, 656 (1887)
[10] Ramsay and Young, Jour. Chem. Soc. (London) **47**, 642, (1885)

756 mm pressure. It was considered unnecessary to distil the amount used for the evaporation, so it was used after being freed from water.

The vapor pressure values were taken from the work of S. Young.[11] These were considered reliable, and were interpolated by plotting the reciprocal of the absolute temperature against the logarithm of the observed vapor pressure and drawing a straight line through the plotted points.

M-xylene (mol. wt. = 106.12). This liquid always contains a slight amount of the ortho and para isomers which cannot be separated by fractional distillation on account of their close boiling points. The material on hand, however, was quite pure and when fractionated through a Hempel column distilled between 139° and 140° C. The total amount was fractionated before being used for the evaporation experiments. It was the only liquid available at the time having a vapor pressure between that of chlorbenzene and nitrobenzene. The only vapor pressure values found in the literature were those determined over a short range by F. Neubeck.[9] These data were plotted and extrapolated to the lower temperatures on a straight line curve.

Nitrobenzene (mol. wt. = 123.08). This liquid was quite pure but was slightly brown in color, so it was freed from water with calcium chloride and distilled through a straight-glass column. It had a constant boiling point of 210° C throughout and its analyses showed a purity of 96.06 per cent. The boiling point given by W. Louguinine[12] is 210.6° C at 760 mm. Since the vapor pressures of nitrobenzene as determined by Kahlbaum,[7] Neubeck,[9] and Marcellin[13] do not extend to room temperature and do not agree in the lower range measured, P. D. Watson of this laboratory measured the vapor pressure very carefully by the boiling point method from atmospheric pressure down to 25 mm and obtained an excellent check with the data of Kahlbaum at high pressures although deviating slightly at the lower pressures. This check is of considerable interest to us since we have used his values for several of the other liquids employed in the evaporation experiments.

The vapor pressures at the temperatures of the evaporation experiments were calculated from the equation $\log P = -3177.307/T - 3.62491 \log T + 19.18057$ in which the constants were evaluated from the following data of Watson for the vapor pressure at 210.7°, 197.7° and 103.0° C: 759.6, 552.0, and 24.8 mm, respectively. This equation reproduces the other data of Watson and that of Kahlbaum above 25 mm. Some ap-

[11] S. Young, Jour. Chem. Soc. (London) **55**, 502 (1889)
[12] W. Louguinine, Ann. Chim. Phys. (7) **27**, 119 (1902)
[13] Marcellin, Comptes Rendus **158**, 1420 (1914)

proximate measurements of the vapor pressure at room temperature were made by Watson using the method of Menzies.[14] These measurements give values that are too high below the room temperature (27.8° C) due to a slight amount of nitrobenzene in the connecting tubing out of the bath, but the value 0.525 mm at 30.1° C is probably fairly accurate and it is seen to agree very well with the value 0.504 mm calculated from the equation above. Press of other work prevented more accurate measurements at the time but these indicate that the values for the vapor pressures at room temperature calculated by the equation based on measurements at higher temperatures are probably very close to the true values although their exact accuracy cannot be stated.

Method of Conducting Measurements

With the evaporating pan in position, the suction fans were started and regulated to the desired velocity requiring about 20 minutes to attain constant readings on the anemometer. The circulating pump was started, the thermometer set in place, and part of the weighed liquid poured into the pan in such a manner as to cover the whole surface at once without splashing. The exact time was noted at the start of evaporation, and the rest of the liquid then carefully added to avoid spillage.

The temperatures, anemometer readings and relative humidity readings were then recorded. The readings were taken as often as was thought necessary, depending upon the fluctuations in temperature of the liquid, i. e. in some cases, the temperature variation was so great that a reading was recorded every 10 or 15 minutes and in others, readings were required only at 30 minute intervals. The length of time for a run depended entirely upon the vapor pressure of the liquid and the capacity of the pans. The wind could be switched off at the exact time required at the end of each experiment by a remote control switch installed under the tunnel.

When the final temperature of a run had been recorded, a small check valve was released in the center of the upper pan, allowing it to drain somewhat. This facilitated handling and weighing of the pans, partly full of liquid. This was usually done about five minutes before time to stop the experiment. The two operators were then in readiness to take down the pan at the instant the fans were cut off. The pump was disconnected and the pan lowered by the rope, until the sliding shaft rested at its lowest position. The key was pulled out of the shaft, releasing the pans, etc. The operators, one on each side of the pan, gently lifted the

[14] Menzies, Jour. Amer. Chem. Soc. **24**, 2218 (1920)

pan off the shaft and very carefully placed it on the balance. From the time the wind velocity was stopped till the actual weight was recorded on the balance, an interval of two to three minutes elapsed; therefore a slight correction might seem necessary on account of the evaporation of the more volatile liquids into still air at this prevailing temperature. In runs 49 and 50 an approximate idea of this correction was experimentally determined for toluene and in run 58 for m-xylene by evaporation in still air. The greatest rate thus obtained is only about 4 grams per minute, hence this loss is within the experimental error of weighing and no correction was made for it in the tabulated data.

This procedure was strictly adhered to in all cases, with the exception of some of the first runs where the liquid used was contained in more than one bottle, thus making the experimental error greater by 3 or 5 extra weighings. Another instance was that of adding more liquid during evaporation. This addition of new liquid sometimes caused a considerable rise in temperature, as noted in the data.

The total possible weighing error in the weight of liquid evaporated is $\pm$ 16 grams using the method of procedure described above. Assuming this error for all runs after No. 12, the per cent error in weighing has been calculated for each run and is recorded with the other data in Table I.

Of the numerous difficulties encountered, the method of weighing the pan after evaporation caused the most serious trouble, but as the operators became more skillful in the technique of handling the apparatus full of liquid, this difficulty was overcome and few losses occurred by spillage.

Throughout the experiments, the temperature of the liquid was kept as uniform as possible by circulating the liquid with a small rotary pump. At all velocities, a ripple was noticed on the surface of the liquid. The main factor during the experiment was that of holding the air to a constant velocity. At the rate of 6 miles per hour or less, it was held to within the maximum variation of 0.5 mile per hour. At higher velocities, it could be held much more constant. It was noticed that outside weather conditions caused an appreciable effect at the lower rates, primarily due to the direction and force of the outside wind at the intake openings of the tunnel. The varying speeds of the motors driving the fans also influenced this to some extent.

During the first experimental runs, the upper pan became slightly warped and no longer sat perfectly level. The corner of a steel plate was placed on the edge of the pan to keep it level during subsequent runs. We did not realize at the time that this plate lying close to the pan might have some effect on our results. It is possible that the variable turbulence

caused by the air flow striking the plate may be the cause of the discrepancy in some of the data. It is also possible that air leakage may have occurred in some cases between the pan and the gasket thus making another error to contend with in our measurements.

Measurement of wind velocity. A Robinson cup anemometer with an e'ectrical contact for every 88 feet was used in the earlier work but was not of sufficient accuracy for our purpose at the low velocities, although it gave very reliable results at velocities above 6 miles per hour.

For the low velocity measurements, i. e. 6 miles per hour or less, a special vane type anemometer made by A. Stroppaine and Company of Berne, Switzerland, was used. The vanes are made of aluminum and the dial which reads in meters projects on an arm. The instrument was calibrated by the makers on a rotating apparatus 10 meters in diameter taking the wind of rotation into consideration. A calibration certificate accompanied the instrument. This was an extremely sensitive instrument and all the readings were taken with it on the windward side of the pan about 2 inches away from the edge on the steel plate. The axis of the vanes was about 2 inches above the surface of the liquid.

Measurements of temperature. Temperature measurement in the pan was taken at the time noted in the experimental data with a 14 inch calibrated thermometer No. 7334, reading in 10ths of a degree and having a range of -10 to $+100°$ C for 3 inch immersion. It was laid almost horizontal across the pan through the hook in the center, the evaporating liquid reaching the 3 inch immersion mark at an angle.

During the first part of the work, a calibrated thermometer was not available, therefore an ordinary chemical thermometer range -5 to $+100°$ C was used in runs 0 to 14. As it was then broken, we were unable to calibrate it and correct the temperature for these runs. An alcohol thermometer of the required range was used in runs 14 to 19. This was afterwards calibrated against the above instrument No. 7334. The corrections was applied to the experimental data before they were inserted in the tables.

The temperature of the air in the tunnel was taken by an ordinary uncalibrated chemical thermometer, ranging from -5 to $+100°$ C, reading in single degrees.

Measurements of relative humidity. The relative humidity was measured with a Tycos hygrodeik and checked at intervals by a sling psychrometer. The wicks of the wet bulb were changed once a month and fresh water was used every day. The relative humidity was not recorded at regular intervals but was taken 2 or 3 times during a run, and in some instances 5 or 6 times, when the moisture content of the air fluctuated.

Barometric pressure. Barometric pressure inside the tunnel was taken with a standard Fortins Barometer, U. S. Weather Bureau type, with a vernier scale reading to 1/10 mm. The pressures are not included in the data, being recorded in only a few runs to determine the pressure change for wind velocities of 6 and 12 miles per hour. The effect is small, amounting to 1/2 mm from normal pressure at 6 miles per hour and an average of 1 mm at 12 miles per hour.

Experimental Data

The essential data for 49 evaporation runs have been condensed into Table I. Some of the runs were spoiled by accidents, generally spillage of the liquid, and the data for these have been omitted. The air temperature was generally fairly constant during a run, and it has not seemed worth while to record all the individual temperature readings, only the average value being given in the table. The liquid temperature has such an important influence on the rate of evaporation that all the individual corrected temperature readings were used in calculating the weighted mean vapor pressure, although only the average temperature of the liquid is included in Table I. Using the vapor pressure data already discussed, the weighted mean vapor pressure has been calculated for each run as follows: The vapor pressure corresponding to each individual liquid temperature reading has been multiplied by the number of minutes elapsed until the next temperature reading and the sum of these products for each run has been divided by the total time of the run in minutes. This weighted mean vapor pressure is recorded in Table I.

In the runs before No. 14 the accuracy of the weights is not known, but it was undoubtedly much less than in the later experiments. The thermometer used in this work was not calibrated and the cup anemometer was used. These first twelve runs, therefore, should not be given as much importance as the later ones.

As mentioned in the description of the tunnel, the wind velocity could only be held constant within about 0.5 miles per hour and although the wind velocities recorded in the table are averages of several readings, regular readings were not made and, consequently, a weighted mean wind velocity cannot be given as in the case of the vapor pressures. There is, therefore, a considerable percentage error attached to the wind velocities recorded in the data, especially for the lower wind velocities.

IV. Discussion of Data

Since the object of this experimental investigation was to determine the relation between rate of evaporation and vapor pressure, the ratio

TABLE I

Experimental Data

Material	Run	Wind velocity (miles/hr)	Av. temp. of air	Av. temp. liquid	Mean vapor pressure P	Evaporation (mols./hr) M	Error of weighings (percent)	$\frac{M}{P}$	Relative Humidity
Nitrobenzene	1	5.9	31.0°C	30.2°C	0.481mm	0.295		0.613	
	2	5.7	32.1	31.8	0.548	0.394		0.719	
	3	6.0	31.0	30.1	0.504	0.336		0.666	
	26	5.6	31.4	31.0	0.568	0.454	5.72	0.799	36
	27	5.8	30.8	28.7	0.462	0.391	6.64	0.846	41
	28	6.0	26.7	26.4	0.381	0.324	8.00	0.850	49
	29	6.4	28.2	26.4	0.387	0.355	9.15	0.917	67
	30	11.9	25.5	24.8	0.346	0.422	5.13	1.220	79
	31	11.67	24.2	25.5	0.361	0.445	5.84	1.233	48
	32	11.8	22.4	22.1	0.284	0.295	8.8	1.039	52
	33	12.2	22.9	22.5	0.295	0.381	5.81	1.292	83
	40	15.0	17.5	17.8	0.217	0.355	9.15	1.636	57
Toluene	6	6.0	27.3	17.6	19.07	13.98		0.733	63
	7	6.0	28.2	19.0	20.55	14.29		0.695	53
	8	6.0	30.2	20.2	21.71	16.03		0.738	45
	11	6.0	26.9	16.6	18.80	14.40		0.766	
	12	6.0	26.3	16.8	19.04	13.90		0.730	52
	14	5.4	22.7	14.3	17.84	11.06	0.725	0.620	61
	16	5.7	31.0	18.8	23.89	17.40	0.333	0.729	66
	17	5.1	37.2	25.3	42.58	22.24	0.39	0.522	45
	18	5.3	30.6	20.2	23.74	16.99	0.341	0.716	64
	19	5.4	34.9	20.4	25.47	21.50	0.269	0.844	50
	20	5.5	29.6	20.5	23.83	17.99	0.483	0.755	72
	42	2.49	15.9	12.7	12.859	7.05	0.616	0.548	56
Toluene	43	3.59	18.5	12.6	14.985	6.14	0.707	0.410	59
	44	2.86	9.6	6.2	11.413	4.26	1.357	0.373	64
	45	6.46	14.0	9.1	11.872	8.50	0.681	0.716	52
	46	3.02	13.0	8.7	10.971	4.74	1.22	0.432	67
	47	3.18	18.8	13.3	15.476	6.07	0.954	0.392	49
	48	2.08	14.2	9.2	12.105	4.45	1.30	0.368	77
	49	0	18.5	18.6	20.921	2.67	1.62	0.1275	88
	50	0	20.2	18.4	20.490	3.24	2.68	0.158	76
	51	2.68	11.9	12.5	14.250	5.88	1.476	0.4125	89
	53	5.03	12.2	10.5	13.00	7.75	1.12	0.596	55
	54	5.55	6.4	6.5	9.539	8.82	0.985	0.924	92
	55	5.65	7.2	7.8	11.322	8.61	1.01	0.760	96
M-xylene	21	5.4	28.6	23.2	8.83	6.89	1.093	0.780	73
	22	5.5	29.3	23.8	8.90	6.61	1.14	0.743	71
	23	5.8	29.1	25.09	9.50	7.05	0.534	0.742	63
	24	5.5	24.6	20.66	7.30	5.62	1.34	0.770	76
	56	2.05	11.0	13.5	4.761	1.71	4.385	0.359	71
	57	2.57	11.6	16.1	5.572	1.96	3.85	0.352	60
	58	0	12.6	17.1	5.860	1.44	6.59	0.246	64
Chlorbenzene	34	5.8	27.2	21.6	9.794	8.04	0.442	0.821	55
	35	6.0	27.7	21.5	9.373	6.60	0.534	0.705	57
	36	12.2	26.1	19.1	8.225	11.00	0.323	1.338	56
	37	12.3	28.3	21.0	9.808	10.71	0.318	1.092	74
	38	6.0	29.6	22.9	10.319	6.70	0.53	0.650	65
	39	6.1	28.8	22.7	10.07	7.56	0.47	0.751	70

of the mols evaporated per hour to the vapor pressure in mm of mercury has been calculated for each run and included in Table I with the data. It is at once apparent that this ratio increases with wind velocity and, consequently, in order to compare the different runs with each other, the ratio has been corrected for wind velocity as follows: In the accompanying figure the ratios of mols evaporated per hour to vapor pressure have been plotted against the wind velocity for all the runs. Inspection of the figure shows that while the experimental errors cause a considerable scattering of the points, the relation between the wind velocity and the ratio of rate of evaporation to vapor pressure may be fairly well repre-

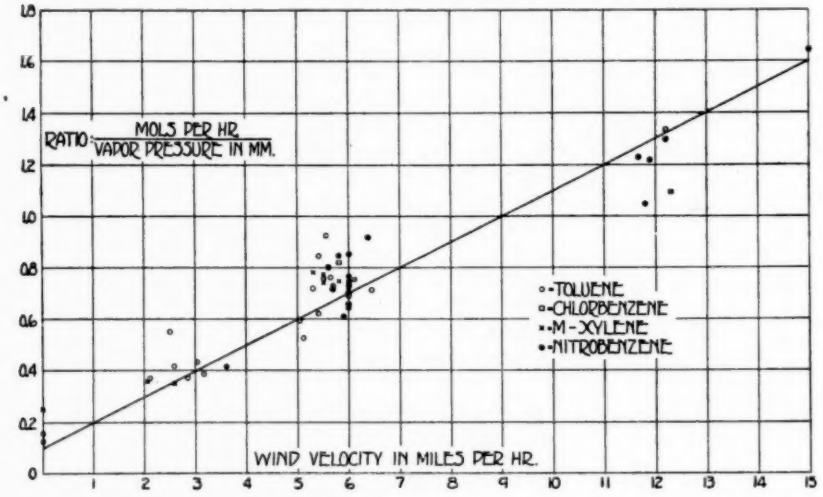

Fig. 1. Ratio of evaporation to vapor pressure as a function of wind velocity.

sented by a straight line. The principal experimental error for most of the points is due to errors in the wind velocity measurements and this is especially true for the low wind velocities. For the runs recorded as zero wind velocity the fans in the tunnel were not run but there was undoubtedly some air movement and consequently more evaporation than would correspond to actual still air. The line has been drawn to give a less value for the ratio at zero wind velocity than the experimental points and to represent the mean of the other points as well as may be. It would have been possible to represent the mean of the experimental values somewhat more closely with a curve but this is hardly justified by the accuracy of the data while the simplicity of the straight line relationship recommends it for use as a first approximation.

The straight line in the figure represents the equation: mols/hour $=(0.1+0.1$ wind velocity in miles/hour)(vapor pressure in mm).

Using this equation the mols per hour evaporated have been calculated for all the experimental runs from the wind velocity and vapor pressure. If we omit the runs for zero wind velocity which are unreliable for the reasons already discussed, the average per cent deviation for the remaining 46 runs, neglecting signs, is 10.72 per cent. The calculated rate of evaporation is greater than the observed for 17 runs, and less than the observed for 29 runs. This agreement between calculated and observed rates of evaporation is remarkably close when we consider the errors involved in the measurements and that we are concerned with 7-fold changes in wind velocity and variations in vapor pressure of 100-fold. Such an agreement is adequate proof that the fundamental relation underlying the calculation is sound and we may conclude as a first approximation that the number of mols of any liquid evaporating into a current of air is proportional to the vapor pressure of the liquid.

CHEMICAL WARFARE SERVICE
WAR DEPARTMENT,
WASHINGTON, D. C.,
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THERMAL DIFFUSIVITY AND CONDUCTIVITY OF SOME SOIL MATERIALS

By L. R. Ingersoll and O. A. Koepp

Abstract

Thermal diffusivities of certain soil materials, quartz sand, sandy clay, calcareous earth and packed snow, have been determined by a method based on the principle of linear heat flow in a slab whose faces are suddenly chilled. The material was packed in a narrow sheet copper box having broad faces, with a resistance thermometer in the center. After standing at room temperature for two days it was placed in stirred ice-water and the time required for the temperature to fall half-way to zero noted. This allowed direct calculation of the diffusivity, and from a knowledge of the density and specific heat, of the conductivity.

WHILE the thermal conductivity of a great variety of soils and rocks has been measured, there are relatively few diffusivities listed, in spite of the fact that in practically all cases of heat flow, save the steady state, it is the latter quantity which directly determines the temperature at any point. Moreover, save in relatively few instances,[1] such diffusivities are not the result of direct determination but are calculated from conductivity measurements by the relation $h^2 = k/cd$, where c is specific heat and d density. The diffusivity h^2 in the present case was measured as follows. The material was packed into a rectangular box of sheet copper, 17.5 cm high, 19.5 cm wide and 8 cm thick. In the center was a resistance thermometer of No. 38 enameled copper wire wound on a piece of mica 2 by 4 cm and covered with marine glue, placed parallel to the broad faces. This was connected with a Leeds and Northrup recorder. To make the heat flow strictly linear and normal to the broad faces, the three narrow sides were lined with paraffined wood 2 cm thick, with a small air space next the copper. The top had a close-fitting cover.

After packing, the box was allowed to stand in a pail of water in a room at reasonably constant temperature for two or three days, or until the recorder showed a long line of steady temperature—about 24° C save for snow, which, of course, was initially below zero. It was then plunged into a large jar filled with cracked ice and water, and this instant was marked as the zero of time on the recorder sheet. In a few minutes the temperature at the center would begin to fall and within an hour, in most cases, would drop half-way down to its final value of 0° C. The fall was

[1] For instance, Y. Tadokoro, Tohoku Univ. Sci. Reports, **10**, 339 (1921)

gradual enough, however, so that there was no appreciable lag on the part of the recorder. During this time the ice water was vigorously stirred, keeping at zero the faces of the box, and therefore of the two surfaces of soil.

It will be seen that we have approximated here the ideal case of linear flow in a slab, initially throughout at the same temperature, whose faces are suddenly lowered to and held at zero. The temperature at the center is given by the equation:[2]

$$\theta = \theta_0 \left\{ 1 - \frac{4}{\pi} e^{-h^2\pi^2 t/l^2} + \frac{4}{3\pi} e^{-9h^2\pi^2 t/l^2} - \cdots \right\}$$

where $l = 8$ cm in this case. For $\theta/\theta_0 = 1/2$, $h^2\pi^2 t/l^2 = 0.935$ and h^2 is calculated accordingly. Values of h^2 calculated on the basis of $\theta/\theta_0 = 1/3$ and $2/3$ were in agreement with those from $\theta/\theta_0 = 1/2$.

The following table lists the results. The conductivities have been calculated from the diffusivities. The densities were measured in all cases, but the specific heats were as far as possible taken from tables.

Material	Percentage moisture	Diffusivity h^2	Specific heat c	Density d	Conductivity K
Quartz sand, medium fine, dry..	0	0.0020	0.19	1.65	0.00063
Same, with water	8.3	0.0034	0.24	1.75	0.0014
Sandy clay.....	15.0	0.0038	0.33	1.78	0.0022
Calcareous earth, water saturated	43.0	0.0019	0.53	1.67	0.0017
Snow, densely packed.....		0.0041	0.50	0.54	0.0011

Where comparison of these values with existing data is possible, the agreement is satisfactory.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF WISCONSIN,
March 4, 1924.

[2] Ingersoll and Zobel, Math. Theory of Heat Conduction, p. 108.

BOOK REVIEWS

Foibles and Fallacies of Science, by DANIEL W. HERING—This book will be appreciated by men of science because of the entertainment which it affords. It can be recommended to readers who make no pretense to a knowledge of general science or to the mastery of any special field thereof, because of the warnings contained in the book to beware of imposters and would-be scientists. Notwithstanding the activities of our scientific men, the great masses of our people have little or no comprehension of the method of science. Opposition to scientific medical research is assuming alarming proportions. A large part of our population would favor legislation against the teaching of evolution. Rain makers still command a comfortable income. What is the cause of this mental flabbiness and this obscurantism in our population? Perhaps the opposition of modern educational theory to rigorous scholastic standards, particularly to the serious study of mathematics, physics, chemistry and foreign languages in secondary schools, may account in part for this deplorable attitude of the popular mind. Any publication such as Hering's book, which contributes to more general enlightenment, is to be welcomed.

Among the topics treated are astrology (ancient and modern), almanacs making weather predictions, transmutation of metals, various perpetual motions including the Keely motor, attacks upon Newton's law of gravitation and the wave theory of sound, the devining rod, palmistry, Symmes' theory that the earth is hollow, the moon hoax of 1835, the Cardiff giant, various prophesies, the actions of charlatans, the elixir of life and the fountain of youth. The book is illustrated and contains a short bibliography at the end of each chapter.

Passages in Hering's book which relate to the history of science are as a rule carefully drawn, but a few statements occur which should not be taken seriously. The sentence, "at the time of Newton and for more than a century after, the corpuscular theory of heat and light prevailed," would be nearer the truth if "at the time of Newton" were omitted. During the seventeenth century many of the leaders (including Descartes, Amontons, Francis Bacon, Newton, Boyle) held that heat was due to motion. As to light, Huygens's and Hooke's wave theory had adherents. Newton himself advanced the emission theory only with great hesitation, as a second hypothesis, and never definitely discarded the wave theory. Newton was able simultaneously to entertain two di tinct hypotheses of light.—Pp. XIII+294. Price $2.50. Van Nostrand, 1924.

FLORIAN CAJORI

Galvanomagnetic and Thermomagnetic Effects. L. L. CAMPBELL.—This book is another of the series of *Monographs of Science* edited by Sir. J. J. Thomson and Professor Frank Horton. In it is given an historical, experimental and theoretical account of the Hall effect and the group of phenomena related to it, including the change of electrical resistance, of thermal conductivity and of Peltier effect, in a magnetic field. There is a full account of the different methods by which these different phenomena and their variation with temperature and with the intensity of the magnetic field have been studied. To this is added a complete compilation and a carefully prepared analysis of the data which have been obtained on metals, alloys, compounds, electrolytes and gases. Excellent tables give in compact form the magnitude of these effects for different temperatures and for different strengths of magnetic field. The brief statements of the theories of these effects serve to show that the existing theories are insufficient and tentative guesses after the truth. At the end is a complete bibliography of the literature bearing on the subject.

The bringing together of the data and results in this field and arranging them in a logical sequence is a valuable contribution, particularly as no detailed account of this group of diverse phenomena had previously been published. The importance of this compilation in connection with the formulation of any theory of the solid state must be recognized. It should be in the hands of all those interested in the electron theory of metals.—Pp. XII+311. Price $5.25. Longmans, Green and Co., 1923. A. W. SMITH

Friction, by T. E. STANTON.—The aim of this book, in the words of the writer, is "the collection in a single volume of the results of modern investigations into the nature and laws of friction." It is the only book written which is devoted entirely to friction and which covers the subject in a comprehensive way; and its author is a recognized authority on this subject, well qualified to write such a book. The subject matter is very similar to that presented by the author in his article on "Friction" in *The Dictionary of Applied Physics.*

The sections on fluid friction, to which more than half of the book is devoted, are of particular scientific value. After an outline of the derivation of the equations of motion of a viscous fluid a study is made for certain simple cases of the critical condition of flow in which turbulence arises. Experimental data are given on turbulent motion for certain cases in which the general law of surface friction, which is believed to hold, receives an interesting confirmation. The important theories of lubricated surfaces are presented with accompanying experimental studies. The remainder of the book is taken up with the subjects of solid friction, rolling friction and the transmission of heat to a fluid passing over a heated solid surface.

The material, though necessarily rather condensed for the most part, is clearly presented. Several small typographical errors in the more mathematical portions require correction.—Pp. 180, Longmans, Green and Co., 1924. ARTHUR L. KIMBALL, JR.

Modern Gypsies. MARY CREHORE BEDELL.—The account of a twelve thousand mile motor camping trip encircling the United States, made with his family by Frederick Bedell, for many years editor of the *Physical Review.* Although it does not deal with physics, the book will have a personal interest for many readers of this journal. It will also appeal to all lovers of out-of-doors, of travel and adventure, for in a simple, straightforward style it gives a continuous series of well selected and interesting details of the people, local customs, and landscape encountered.—Pp. 262, 35 illustrations. Brentano's, 1924.

CORRECTIONS

FREE CONVECTION OF HEAT IN LIQUIDS. Roy A. Nelson. Vol. 23, 94-103, January, 1924.—On p. 101 the statement that A. H. Davis in his article in Phil. Mag. **44**, 920, 1922, had assumed the heat loss per unit length to be proportional to θ^2, is incorrect. In fact his formula No. 18 indicates that n lies between the limits given by the author. The mistake, which was pointed out by Mr. Davis, does not affect the conclusions of the paper but did an injustice to Mr. Davis which is sincerely regretted.

A graphical method for the utilization of rotation spectra in crystal structure determination. Maurice L. Huggins. Vol. 23, 663, abstract 4, May, 1924,—The first equation should read

$$x=\frac{\sin\lambda\sqrt{(h^2/a^2+k^2/b^2)-\frac{1}{4}n^2\lambda^2(h^2/a^2+k^2/b^2+l^2/c^2)^2}}{1-\frac{1}{2}n^2\lambda^2(h^2/a^2+k^2/b^2+l^2/c^2)}.$$